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Mechanism and Rates of the Gas Phase
Oxidations of Sulfur Dioxide and the
Nitrogen Oxides in the Atmosphere

Ohio State Univ., Columbus. Dept. of Chemistry

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by

Jack G. Calvert and William R. Stockwell
National Center for Atmospheric Research
P. O. Box 3000
Boulder, CO 80307

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EPA Project Officer
Joseph J. Bufalini

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT As our knowledge of the atmospheric chemistry of the SO ₂ , NO, and NO ₂ continues to grow, it becomes increasingly clear that many different chemical reactions contribute to the oxidation of these oxides in the atmosphere. Solution phase and gas phase chemistry are both important to "acid rain" development, and gas-solid, gas-liquid, liquid-solid as well as simple gaseous molecule interactions are seemingly important in some circumstances as well. This chapter reviews critically the current evidence as to the nature of the homogeneous, gas phase reactions which are important in the atmospheric oxidation of SO ₂ , NO, and NO ₂ . At first sight the delineation of the homogeneous chemistry of these oxides appears to be one of the simplest of the many tasks faced by atmospheric scientists concerned with "acid rain" control. The evaluation of the mechanism and rates of solution phase and heterogeneous pathways for SO ₂ and NO _x oxidation within the troposphere, the significance of surface removal processes, and the transport and diffusion processes are much less amenable to simple laboratory studies and quantification. Although a significant wealth of important and necessary information related to SO ₂ and NO _x chemistry has been defined in recent years and a reasonable depth of knowledge of the many fundamental gas phase processes exists today, many uncertainties still remain in this, the "simplest" of the research areas related to "acid rain" development.		
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The Mechanism and Rates of the Gas Phase Oxidations of Sulfur Dioxide and the Nitrogen Oxides in the Atmosphere

Jack G. Calvert and William R. Stockwell

I. INTRODUCTION

Scientists recognize today that the development of sound and lasting strategies for the control of "acid rain" will require quantitative inputs from a variety of different disciplines. We must be concerned with not only the emission rates for sulfur and nitrogen oxides, but the nature of the chemical mixtures of the other atmospheric impurities with which these species interact. We must identify the nature and the rates of the various SO_2 and NO_x oxidation steps, as well as the physical processes which transfer the gases and aerosols about the atmosphere and those that remove them from it. As our knowledge of the atmospheric chemistry of the SO_2 , NO , and NO_2 continues to grow, it becomes increasingly clear that many different chemical reactions contribute to the oxidation of these oxides in the atmosphere. Solution phase and gas phase chemistry are both important to "acid rain" development, and gas-solid, gas-liquid, liquid-solid as well as simple gaseous molecule interactions are seemingly important in some circumstances as well. Observations of the nature of the dominant end products of these reactions in the atmosphere, H_2SO_4 , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, HNO_3 , NH_4NO_3 , etc. give few clues as to the pathways through which SO_2 and NO_x oxidations occur. Yet for predictive model development we require a knowledge of the elementary chemical steps which are involved, since it is the rates of these reactions which follow well-defined mathematical laws which are expressed in terms of reactant concentrations, temperature, pressure, etc.

In this chapter we will review critically the current evidence as to the nature of the homogeneous, gas phase reactions which are important in the atmospheric oxidation of SO_2 , NO , and NO_2 . At first sight the delineation of the homogeneous chemistry of these oxides appears to be one of the simplest of the many tasks faced by atmospheric scientists concerned with "acid rain" control. The evaluation of the mechanism and rates of solution phase and heterogeneous pathways for SO_2 and NO_x oxidation within the troposphere, the significance of surface removal processes, and the transport and diffusion processes are much less amenable to simple laboratory studies and quantification. Although a significant wealth of important and necessary information related to SO_2 and NO_x chemistry has been defined in recent years and a reasonable depth of knowledge of the many fundamental gas phase processes exists today, many uncertainties still remain in this, the "simplest" of the research areas related to "acid rain" development.

We will begin our discussion with a consideration of the atmospheric chemistry of SO_2 , its photochemistry and its thermal reactions with various reactive species present in the atmosphere.

II. THE POTENTIAL ATMOSPHERIC REACTIONS OF ELECTRONICALLY EXCITED SO_2

Sulfur dioxide absorbs light within the ultraviolet region of the solar radiation incident within the troposphere. See Figure 1. Note there is a significant overlap between the actinic flux incident within the lower troposphere and two distinct absorption regions of SO_2 . Excitation within the "forbidden," long-wavelength band forms the excited $\text{SO}_2(^3\text{B}_1)$ species, while excitation at the wavelengths below 3300Å generates higher excited states, presumably the $^1\text{A}_2$ and $^1\text{B}_1$ species.

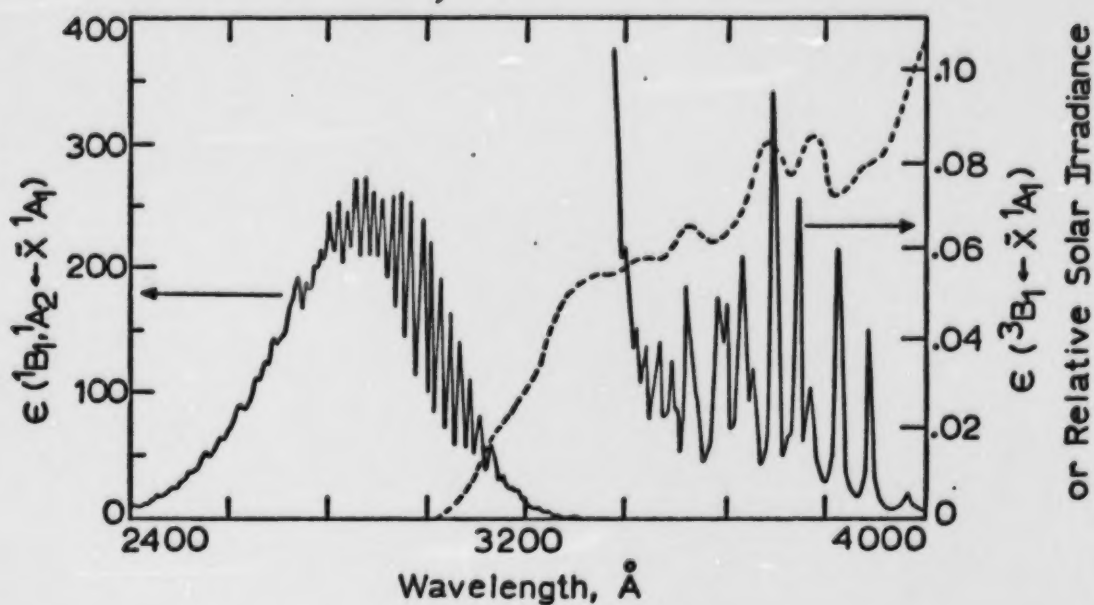
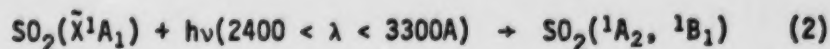
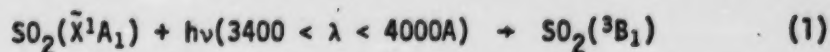
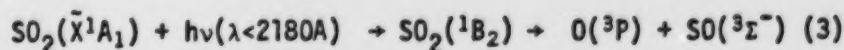


Figure 1. Comparison of the extinction coefficients of SO_2 within the first allowed band (left), the "forbidden" band (right), and a typical distribution of the flux of solar quanta (relative) at ground level (dashed curve).



All of these excited states of SO_2 are non-dissociative; only quanta of light at wavelengths below 2180Å (not present in the troposphere) provide sufficient energy to allow photodissociation:

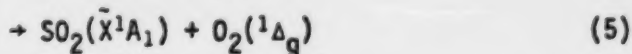
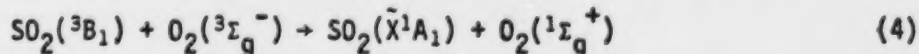


The lower excited singlet states of $\text{SO}_2(^1\text{A}_1, ^1\text{B}_1)$ appear to be very short lived in air at 1 atm, and they are rapidly converted by collisional perturbations to $\text{SO}_2(^3\text{B}_1)$ molecules, possibly $\text{SO}_2(^3\text{A}_2)$ and $\text{SO}_2(^3\text{B}_2)$ molecules, and ground state $\text{SO}_2(\tilde{X}^1\text{A}_1)$ molecules. The rate of excitation of SO_2 through sunlight absorption can be very significant. If this excitation were the rate determining step in the photooxidation of SO_2 , that is, if every SO_2 excited were oxidized through subsequent reaction with O_2 or other reactants, then the lifetime of SO_2 in the lower troposphere with overhead sun should be as low as 52 min.² Of course this is not the case. The $\text{SO}_2(^3\text{B}_1)$ species appears to be one of the most favored states which is ultimately populated through sunlight absorption and collisional processes in the lower atmosphere. The reactions of this species with various atmospheric gases and many atmospheric impurities have been studied extensively. Some of these reactions which relate to possible processes of significance in the troposphere are summarized in Table I. Of course the rates of these bimolecular reactions depend on a product of the reactant concentrations and the appropriate rate constant. Quenching of $\text{SO}_2(^3\text{B}_1)$ by the atmospheric gases are the

Table I. The $\text{SO}_2(^3\text{B}_1)$ "Chemical" Quenching Rate Constants for Various Atmospheric Components and Impurity Species in the Overall Reactions Shown

Reactant	Reactions	k , $\text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$	Reference
Oxygen	$\text{SO}_2(^3\text{B}_1) + \text{O}_2 \xrightarrow{(\text{O}_2)} \text{SO}_4 + \text{SO}_3 + \text{O}_3$	} $< 3 \times 10^{-15}$	1
	$\text{SO}_2(^3\text{B}_1) + \text{O}_2 \rightarrow \text{SO}_3 + \text{O}(^3\text{P})$		
	$\text{SO}_2(^3\text{B}_1) + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}_2(^1\Delta_g, ^1\Sigma_g^+)$		2
Sulfur Dioxide	$\text{SO}_2(^3\text{B}_1) + \text{SO}_2 \rightarrow \text{SO}_3 + \text{SO}(^3\Sigma^-)$	7.0×10^{-14}	3
Nitric Oxide	$\text{SO}_2(^3\text{B}_1) + \text{NO}(^2\Pi) \rightarrow ^2(\text{SO}_2\text{-NO}) \rightarrow \text{SO}_2 + \text{NO}(^2\Pi)$	1.3×10^{-10}	2
Carbon Monoxide	$\text{SO}_2(^3\text{B}_1) + \text{CO} \rightarrow \text{SO}(^3\Sigma^-) + \text{CO}_2$	4.3×10^{-15}	4,5
Acetylene	$\text{SO}_2(^3\text{B}_1) + \text{C}_2\text{H}_2 \rightarrow (?) \rightarrow \text{CO} + \text{Other Products}$	2.7×10^{-12}	6
cis-2-Butene	$\text{SO}_2(^3\text{B}_1) + \text{cis-C}_4\text{H}_8 \rightarrow ^3(\text{SO}_2\text{-C}_4\text{H}_8) \rightarrow \text{trans-C}_4\text{H}_8 + \text{cis-C}_4\text{H}_8$	2.2×10^{-10}	7,8
Isobutane	$\text{SO}_2(^3\text{B}_1) + \text{iso-C}_4\text{H}_{10} \rightarrow \text{HOSO} + \text{C}_4\text{H}_9$	1.4×10^{-12}	9,10,11

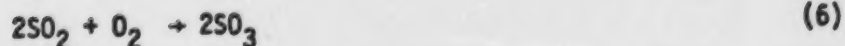
dominant processes which we expect to occur; in air at 1 atm, 25°C, and 50% relative humidity, quenching by N₂, O₂, H₂O, and Ar will occur: 45.7, 41.7, 12.2, and 0.3% of the time, respectively. The quenching by impurity gases is very improbable. Even when these are present at the ppm level the rates of SO₂ conversion by such species are very slow.¹ All available evidence suggests that the only significant chemical result of the major quenching reactions of SO₂(³B₁) occurs with O₂, and this does not lead efficiently to any overall chemical change in the SO₂, but low-lying, excited electronic states of molecular oxygen, O₂(¹Δ_g) and O₂(¹Σ_g⁺), are formed by energy transfer.



These reactions are not unique sources of the excited oxygen, but these species are formed in other atmospheric reactions of much higher rate.¹ Thus we conclude that the photooxidation of SO₂ in the atmosphere through direct excitation by light absorption in SO₂ is not an important source of acids in the atmosphere.

II. THE GENERATION OF REACTIVE MOLECULES AND TRANSIENT SPECIES IN THE TROPOSPHERE

The thermodynamic properties of the oxides of sulfur indicate that sulfur dioxide has a strong tendency to react with oxygen in the air under normal tropospheric conditions.



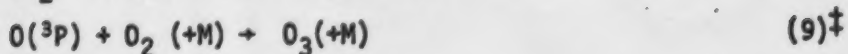
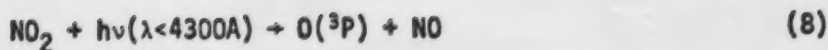
Thus the ratio of $[\text{SO}_3]/[\text{SO}_2] = 8 \times 10^{11}$ at equilibrium in air at 1 atm and 25°C. Thermodynamics also tells us that at normal humidities encountered in the lower troposphere, the SO_3 product of reaction 6 will be converted largely to sulfuric acid, $\text{H}_2\text{SO}_4(\text{aq})$, at equilibrium.



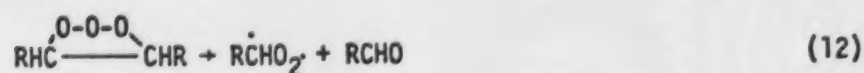
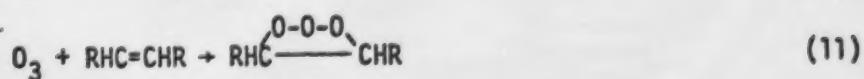
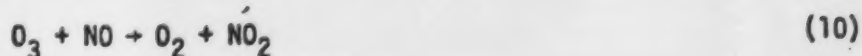
The reaction of SO_3 with H_2O is so fast that any process in which SO_3 is formed in the moist atmosphere can be considered equivalent to the formation of H_2SO_4 . We have seen in previous chapters that certain metal ions (Mn^{++} , etc.) in aqueous solutions of $\text{SO}_2(\text{HSO}_3^-)$ can catalyze the overall sequence of reactions 6 and 7. However reaction 6 is so slow under catalyst-free conditions in the gas phase that it can be neglected as a source of sulfuric acid generation in our atmosphere.

It may be surprising to those unfamiliar with atmospheric reactions to find that most of the gas phase tropospheric chemistry of SO_2 , NO , NO_2 , and other impurity molecules involves their reactions with a variety of reactive, excited molecules, atoms, and free radicals (neutral fragments of stable molecules) which are generated by photochemical and thermal reactions initiated by sunlight absorption by trace gases in the atmosphere. As a background to our further considerations in this chapter we will review briefly here some of this important chemistry.

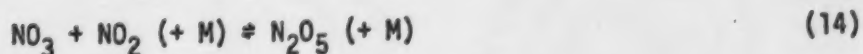
In the polluted troposphere nitrogen dioxide is dissociated by sunlight absorption ($\lambda < 4300\text{\AA}$) to form reactive, ground state oxygen atoms, $\text{O}(^3\text{P})$, and NO in reaction 8, while the O -atom reacts rapidly to form O_3 in 9:



Ozone can reoxidize NO to NO₂ in 10 or react with alkenes to give highly reactive ozonides in 11 and Criegee intermediates in 12.

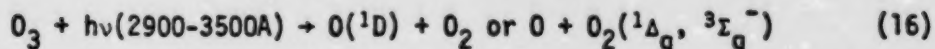
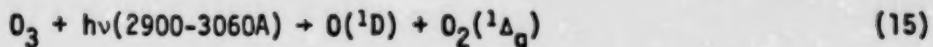


It can also oxidize NO₂ to the reactive transient NO₃ in 13, and this can lead to N₂O₅ in 14:



[†]M shown in this and other equations throughout this chapter designates any other gaseous molecule (usually N₂, O₂, or H₂O in air) which collides with a newly formed molecule such as O₃ in 9, removes some of its excess energy which was released as the new bond formed, and hence prevents the redissociation of the O₃. The rates of the reactions such as 9 which occur by the combination of two simple species and lead to the formation of a simple molecule show a dependence on pressure which reflects the role of the stabilizing collision with M on the reaction. When there is a direct proportionality between the added gas concentration and the rate of the reaction, the reaction is in the third order region (low pressures). When the collision rate becomes great enough at high pressures so that deactivation of the excited molecules occurs during the normal lifetime of the excited molecule, then the reaction becomes second order, and the effect of increased concentration of M is not seen. Many of the important reactions of SO₂ and NO₂ which we will consider in this chapter are in the transition region between second and third order for the condition of pressure encountered in the troposphere. For such reactions rather complex equations are necessary to describe the dependence of the rate constant on M; for example, see equation 124.

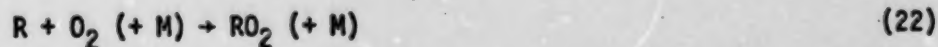
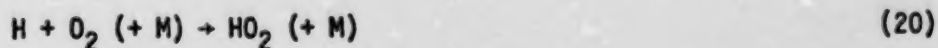
The photodecomposition of ozone may generate electronically excited O-atoms, $O(^1D)$, and excited molecular oxygen with sunlight absorption at the short wavelength region of the spectrum:



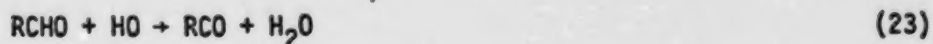
The $O(^1D)$ species formed in 15 is much more reactive than the ground state O-atoms ($O(^3P)$ or often simply symbolized by O). It reacts efficiently when it collides with a water molecule to form a highly important transient in atmospheric chemistry, the hydroxy radical, HO:



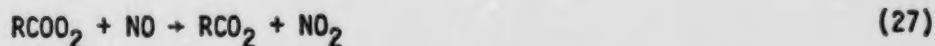
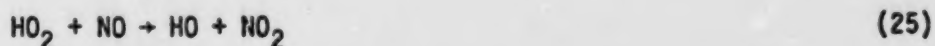
This radical, unlike many molecular fragments formed from carbon-containing molecules, is unreactive toward oxygen, and it survives to react with most atmospheric impurities such as the hydrocarbons, aldehydes, NO, NO_2 , SO_2 , CO, etc. Its reactions with carbon monoxide and the hydrocarbons (RH) lead to another important class of reactive transients, the peroxy radicals:



Here R represents the alkyl groups such as methyl (CH_3), ethyl (C_2H_5), or other larger group derived from the parent hydrocarbons, methane (CH_4), ethane (C_2H_6), or larger hydrocarbon (RH), respectively. The reaction of the HO-radical with aldehydes (RCHO) forms the acyl (RCO) and acylperoxy (RCOO_2) radicals in similar reactions:



The peroxy radicals react rapidly with NO to form NO_2 and another class of reactive species. In the case of the HO_2 -NO reaction HO is regenerated, while with the RO_2 and RCOO_2 radicals, alkoxy (RO) and acyloxy (RCO_2) radicals, respectively, are formed:



The most common fate of the smaller alkoxy radicals in the lower atmosphere is reaction with oxygen. This leads to HO_2 radicals and a carbonyl compound. For example, with the simplest alkoxy radical, methoxy (CH_3O) the following reaction occurs:

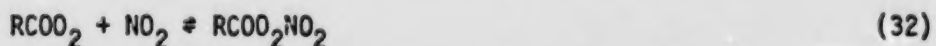


The RCO_2 radicals are of short lifetime, they decompose to form an alkyl radical (R) and CO_2 , with the subsequent generation of another peroxyalkyl radical:



If one combines the occurrence of reactions 12-24 with the reactions 25-29 he has the elements of a chain reaction. That is a single initial HO-radical may oxidize CO, hydrocarbon, or aldehyde, and additional HO-radicals will be regenerated as NO is oxidized to NO₂, and the subsequent steps occur again and again in a repeating cycle of events. The peroxy radicals and ozone are the principle oxidizing agents for NO in the lower atmosphere (reactions 13, 25-27).

When peroxy radicals react with NO₂ an additional class of highly reactive compounds are generated, the peroxy nitrates.



Peroxy nitric acid formed in 30 and the alkylperoxynitrates formed in 31 are relatively unstable in the lower troposphere at the temperatures common to the summer months; they dissociate readily to reform peroxy radicals and NO₂. However during the cold winter months or in the stratosphere they can act as temporary sinks for HO₂ and RO₂ radicals and NO₂.

The singlet delta excited molecular oxygen, O₂(¹Δ_g), a product of reaction 15 and 16, and excited singlet sigma oxygen, O₂(¹Σ_g⁺), product of reaction 4, can be created as well by direct sunlight absorption by

atmospheric O_2 and by energy transfer reactions from other photoexcited species such as $NO_2(\lambda > 4300\text{\AA})$ and excited triplet aromatic hydrocarbons.

It is unimportant for the present purposes of our discussion to consider the complex array of interactions which occur between the several reactive species outlined here and with the various atmospheric impurities. It suffices to say that many aspects of tropospheric chemistry including photochemical "smog" and ozone generation, depend on these happenings.¹² However it is important here for us to evaluate the potential significance of the reactions of the many highly reactive transient species of the atmosphere in oxidizing SO_2 and NO_2 to acids. We will evaluate these reactions for SO_2 in the next section of this chapter.

IV. THE ATMOSPHERIC OXIDATION OF SO_2 BY REACTIVE TRANSIENT SPECIES

There are a large number of potentially significant gas phase reactions of the reactive transients leading to oxidation of SO_2 in the troposphere. These are summarized in Table II. These reactions pass the first test which we often apply in our evaluation. The potential candidate reactions must have the thermodynamic potential to occur. This can be measured qualitatively by the sign of the enthalpy change (ΔH°) for the overall reaction. If this is negative, that is heat is released as the reaction occurs at constant pressure, then this could be an indication of a low activation energy barrier and a reasonably fast reaction. If ΔH is highly positive for a given reaction, then the activation energy will be large and the reaction necessarily slow. Although a negative or small positive ΔH is a necessary condition, it is not sufficient to establish the significance of the reaction. Equilibrium

Table II. Enthalpy Changes and Recommended Rate Constants for Potentially Important Reactions of Ground State SO_2 and SO_3 Molecules in the Lower Atmosphere

Reaction	$-\Delta H^\circ_a$ kcal mole $^{-1}$ (25°C)	$k, {}^b \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$
(32) $\text{O}_2(^1\Delta_g) + \text{SO}_2 \rightarrow \text{SO}_4(\text{biradical; cyclic})$	-25, -28	3.9 x 10 $^{-20}$
(34) $\text{O}_2(^1\Delta_g) + \text{SO}_2 \rightarrow \text{SO}_3 + \text{O}(^3\text{P})$	-13.5	
(35) $\text{O}_2(^1\Delta_g) + \text{SO}_2 \rightarrow \text{O}_2(^3\Sigma_g^-) + \text{SO}_2$	22.5	
(36) $\text{O}_2(^1\Sigma_g^+) + \text{SO}_2 \rightarrow \text{SO}_4(\text{biradical; cyclic})$	-40, -43	6.6 x 10 $^{-16}$
(38) $\text{O}_2(^1\Sigma_g^+) + \text{SO}_2 \rightarrow \text{SO}_3 + \text{O}(^3\text{P})$	1.5	
(39) $\text{O}_2(^1\Sigma_g^+) + \text{SO}_2 \rightarrow \text{SO}_2 + \text{O}_2(^1\Delta_g)$	15.0	
(40) $\text{O}(^3\text{P}) + \text{SO}_2 (+\text{M}) \rightarrow \text{SO}_3 (+\text{M})$	83.0	5.7 x 10 $^{-14}$
(41) $\text{O}_3 + \text{SO}_2 \rightarrow \text{O}_2 + \text{SO}_3$	57.6	<8 x 10 $^{-24}$
(42) $\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3$	9.9	8.8 x 10 $^{-30}$
(43) $\text{NO}_3 + \text{SO}_2 \rightarrow \text{NO}_2 + \text{SO}_3$	32.6	<7 x 10 $^{-21}$
(44) $\text{ONOO} + \text{SO}_2 \rightarrow \text{NO}_2 + \text{SO}_3$	-30	<7 x 10 $^{-21}$
(45) $\text{N}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{N}_2\text{O}_4 + \text{SO}_3$	24.0	<4 x 10 $^{-23}$
(46) $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HO} + \text{SO}_3$	16.7	<1 x 10 $^{-18}$
(47) $\text{HO}_2 + \text{SO}_2 (+\text{M}) \rightarrow \text{HO}_2\text{SO}_2 (+\text{M})$	-7	
(48) $\text{CH}_3\text{O}_2 + \text{SO}_2 \rightarrow \text{CH}_3\text{O} + \text{SO}_3$	-27	<1 x 10 $^{-18}$
(49) $\text{CH}_3\text{O}_2 + \text{SO}_2 (+\text{M}) \rightarrow \text{CH}_3\text{O}_2\text{SO}_2 (+\text{M})$	-31	-1.4 x 10 $^{-14c}$
(50) $(\text{CH}_3)_3\text{CO}_2 + \text{SO}_2 \rightarrow (\text{CH}_3)_3\text{CO} + \text{SO}_3$	-26	<7.3 x 10 $^{-19}$
(51) $(\text{CH}_3)_3\text{CO}_2 + \text{SO}_2 \rightarrow (\text{CH}_3)_3\text{CO}_2\text{SO}_2$	-30	
(52) $\text{CH}_3\text{COO}_2 + \text{SO}_2 \rightarrow \text{CH}_3\text{CO}_2 + \text{SO}_3$	-33	<7 x 10 $^{-19}$
(53) $\text{CH}_3\text{COO}_2 + \text{SO}_2 \rightarrow \text{CH}_3\text{COO}_2\text{SO}_2$	-37	
(85) $\text{HO} + \text{SO}_2 (+\text{M}) \rightarrow \text{HOSO}_2 (+\text{M})$	-37	1.1 x 10 $^{-12}$
(114) $\text{CH}_3\text{O} + \text{SO}_2 (+\text{M}) \rightarrow \text{CH}_3\text{OSO}_2 (+\text{M})$	-24	-5.5 x 10 $^{-13}$

Table II (Continued)

Reaction	$-\Delta H^\circ$, kcal mole ⁻¹ (25°C)	k , ^b cm ³ mole ⁻¹ sec ⁻¹
(63) $\text{RCH} \begin{smallmatrix} \text{O} \text{---} \text{O} \text{---} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{CHR} + \text{SO}_2 \rightarrow 2\text{RCHO} + \text{SO}_3$	-69	See text
$\text{RCH} \begin{smallmatrix} \text{O} \cdot \\ \diagup \end{smallmatrix} \text{CHR} \begin{smallmatrix} \text{O} \text{---} \text{O} \cdot \\ \diagdown \end{smallmatrix} + \text{SO}_2 \rightarrow 2\text{RCHO} + \text{SO}_3$	-89	See text
(64) $\text{R}\dot{\text{C}}\text{HOO}\cdot + \text{SO}_2 \rightarrow \text{RCHO} + \text{SO}_3$	-79	$k_{64}/k_{66} = 6 \times 10^{-5}$ (R = CH ₃)
(66) $\text{R}\dot{\text{C}}\text{HOO}\cdot + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{H}_2\text{O}$	-121	
(65) $\text{RCHO} \begin{smallmatrix} \text{O} \cdot \\ \diagup \end{smallmatrix} + \text{SO}_2 \rightarrow \text{RCHO} + \text{SO}_3$	-58	$k_{65}/k_{68} = 4$ (R = H)
(68) $\text{RCHO} \begin{smallmatrix} \text{O} \cdot \\ \diagup \end{smallmatrix} + \text{CH}_2\text{O} \begin{smallmatrix} \text{O} \cdot \\ \diagup \end{smallmatrix} \rightarrow \text{RCHOCH}_2\text{O}\cdot$	-12	
$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	24.8	9.1×10^{-13}

^aEnthalpy change estimates were derived from the data of Benson,⁹¹ Harding and Goddard,¹²⁶ and Domalski.¹²⁷

^bThe rate constants are all expressed as second order reactions for 1 atm of air at 25°C; see the text for the references to the original literature.

^cThe reverse reaction is so fast that the rate of oxidation of SO₂ through 49 is very dependent on alternate fates of the CH₃O₂SO₂ species; see the text.

thermodynamics tells us nothing about the rates of chemical processes, and the rate of the reaction must be fast as well. The initial identification of the potentially significant reactants through the sign of ΔH must be followed with the determination of the elementary rate constants for these reactions. Then these data, coupled with estimates of the concentrations of the transients in the atmosphere, allow us to evaluate the significance of each reactant in oxidizing SO_2 in the atmosphere. We will consider each of the reactions in Table II with this end in view.

A. SO_2 Oxidation by the Reactive Oxygen Transients

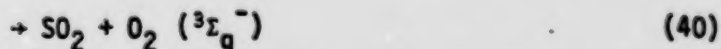
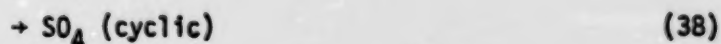
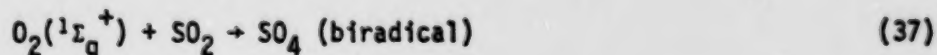
The excited molecular oxygen species, $\text{O}_2(^1\Delta_g)$ occurs in the atmosphere at significant concentrations; theoretical estimates suggest the $[\text{O}_2(^1\Delta_g)] = 10^8 \text{ molec cm}^3$ in a sunlight-irradiated, polluted troposphere.¹² The overall quenching rate constant for $\text{O}_2(^1\Delta_g)$ by SO_2 was measured by Penzhorn et al.¹³ to be $(3.9 \pm 0.9) \times 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. Several channels of reaction with SO_2 should be considered:



The reaction 35 is not likely to be important since it involves a spin inversion and is endothermic by $13 \text{ kcal mole}^{-1}$. In theory the product SO_4 species of 33 and 34 can exist either in a biradical form with near equivalent S-O bonds or in a cyclic, singlet structure involving an

$\text{O}-\text{S}-\text{O}$ linkage.¹⁴ However there is no experimental evidence which supports the occurrence of reactions 33 and 34,¹ and it appears likely to us that reaction 36 is the major channel for $\text{O}_2(^1\Delta_g)$ quenching by SO_2 . In any case the rate and concentration data suggest that the total rate of quenching of $\text{O}_2(^1\Delta_g)$ by SO_2 in the atmosphere amounts to an insignificant conversion of SO_2 ($< 10^{-6}\%$ hr^{-1}).

The $\text{O}_2(^1\Sigma_g^+)$ species is also an unimportant reactant for SO_2 although several channels of reaction are possible in theory:



When one couples the theoretical estimate of $[\text{O}_2(^1\Sigma_g^+)] = 6 \times 10^2 \text{ molec cm}^{-3}$ with the total measured $\text{O}_2(^1\Sigma_g^+)$ quenching rate constant with SO_2 , $k_{37-40} = 6.6 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$, an insignificant maximum rate of SO_2 oxidation by $\text{O}_2(^1\Sigma_g^+)$ is found, $\sim 10^{-7}\%$ hr^{-1} . Obviously both $\text{O}_2(^1\Delta_g)$ and $\text{O}_2(^1\Sigma_g^+)$ are unimportant oxidants for SO_2 in the troposphere.

The $\text{O}(^3\text{P})$ -atom does react readily to oxidize SO_2 in reaction 41:

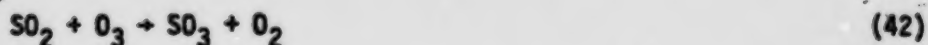


Combining the data of Westenberg and de Haas¹⁶ for this reaction with $\text{M} = \text{N}_2$ and that of Mulcahy et al.¹⁷ for $\text{M} = \text{O}_2$, we estimate a value of the apparent second order rate constant, $k_{41} = (5.7 \pm 0.5) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1}$

sec^{-1} for air at 1 atm and 25°C. In the usual polluted atmosphere the $\text{O}(^3\text{P})$ concentration is roughly proportional to the NO_2 concentration. Whenever $[\text{NO}_2]$ is high, the rate of O-atom generation is high through the NO_2 photolysis reaction 8. The dominant loss reaction for $\text{O}(^3\text{P})$ in the troposphere is through the rapid reaction with molecular oxygen (reaction 9), so that the steady state concentration of $\text{O}(^3\text{P})$ is low in the troposphere, typically below $2 \times 10^5 \text{ molec cm}^{-3}$.⁸ This results in a maximum rate of SO_2 oxidation of about 10^{-2} of hr^{-1} in the sunlight-irradiated, NO_x -polluted troposphere. However for the special case of stack gases at relatively high concentrations of impurities, a burst in SO_3 formation from reaction 41 is anticipated during the early stages of dilution of the stack gases.¹ Thus, if the concentrations of impurities shortly after release from a stack were: NO , 500; SO_2 , 500; NO_2 , 20; O_2 , $1 \times 10^5 \text{ ppm}$, then the instantaneous rate of SO_2 oxidation through reaction 40 alone can be as high as $1.4\% \text{ hr}^{-1}$. As plume dilution with air occurs by factors of 4, 8, 16, and 32, the instantaneous rate of reaction 41 falls quickly to 0.43, 0.20, 0.10, and $0.05\% \text{ hr}^{-1}$, respectively.

One anticipates that the possible $\text{O}(^1\text{D})$ -atom oxidation of SO_2 [$\text{O}(^1\text{D}) + \text{SO}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M}$] to be unimportant in view of the very low $[\text{O}(^1\text{D})]$ in the troposphere and the very rapid competitive reactions of $\text{O}(^1\text{D})$ with O_2 , N_2 and H_2O gases.

The oxidation of SO_2 by O_3 is a highly exothermic reaction ($\Delta H = -57.8 \text{ kcal mole}^{-1}$). Yet the upper limit to the



gas phase rate constants ($k_{42} \approx 8 \times 10^{-24} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$)¹⁸ and the maximum levels of O_3 encountered in photochemical smog ($\sim 5 \times 10^{12} \text{ molec cm}^{-3}$) results in insignificant SO_2 oxidation through 42, $< 1.4 \times 10^{-5} \% \text{ hr}^{-1}$.

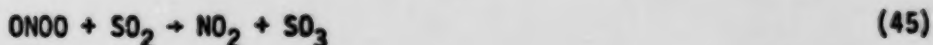
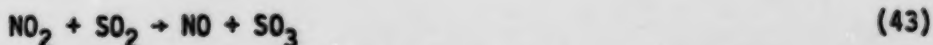
In summary, the current kinetic data related to the reactive oxygen species, $\text{O}_2(^1\Delta_g)$, $\text{O}_2(^1\Sigma_g^+)$, $\text{O}(^3\text{P})$, $\text{O}(^1\text{D})$, and O_3 , reaction with SO_2 and the theoretical estimates of their concentrations point to their unimportance in the SO_2 gas phase oxidation in the troposphere. For the highly unusual conditions which occur in the early stages of stack gas dilution in air, the $\text{O}(^3\text{P})$ - SO_2 reaction can provide rather high instantaneous rates of SO_2 oxidation. However these rates do not last, but fall quickly to values usually less than $10^{-2} \% \text{ hr}^{-1}$ as dilution occurs.

B. The Atmospheric Oxidation of SO_2 through Reactions of the N_xO_y Species

The oxides of nitrogen, NO_2 , NO_3 , N_2O_5 , and $\text{ONOO}^\dagger$ are potential

[†]The ONOO species is presumably the intermediate formed in the NO-O_2 interactions and which is in equilibrium with NO and O_2 in the air. It may be the actual reactant which oxidizes NO in the third-order overall reaction, $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. The species described as NO_3 here is the symmetrical oxide which is formed in the $\text{O}_3\text{-NO}_2$ reaction 13.

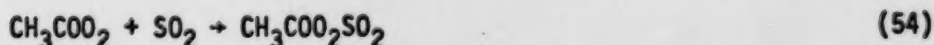
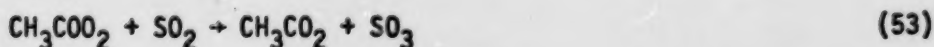
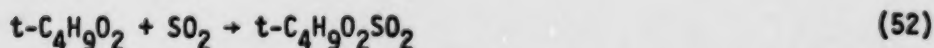
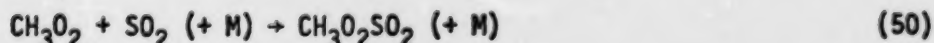
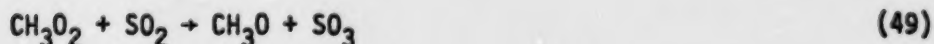
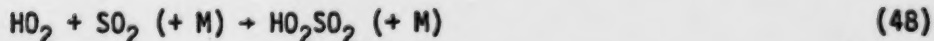
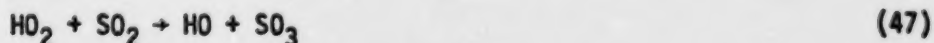
oxidizers of SO_2 in the atmosphere. The potential reactions are all somewhat exothermic; see Table II.



However kinetic data for the reactions 43,¹⁹ 44,^{18,20} 45,¹ and 56,^{18,20} coupled with reasonable estimates for the atmospheric concentrations of these reactive species,^{1,8} $[\text{NO}_2] = 5 \times 10^{12}$; $(\text{NO}_3) = 2.5 \times 10^7$; $[\text{OONO}] = 1.5 \times 10^{11}$; $[\text{N}_2\text{O}_5] = 2.5 \times 10^9 \text{ molec. cm}^{-3}$, gives rates of SO_2 oxidation for NO_2 , NO_3 , ONOO , and N_2O_5 which are insignificant: 1.6×10^{-11} , 6.3×10^{-8} , 3.8×10^{-4} , $3.6 \times 10^{-8} \text{ hr}^{-1}$, respectively.

C. The Atmospheric Oxidation of SO_2 by Peroxy Radicals

The several types of peroxy radicals known to be important in the chemistry of the polluted atmosphere, in the oxidation of NO to NO_2 in particular (reactions 25-27), in view of their favorable thermochemistry could be good reactants for SO_2 in the atmosphere.



The first studies of the HO_2 - SO_2 reaction, based on a competitive reaction scheme, lead to an estimate of $k_{47} = (8.7 \pm 1.3) \times 10^{-16} \text{ cm}^3$

molec⁻¹ sec⁻¹;²¹ this combined with the relatively large concentration of HO₂-radicals estimated for the polluted troposphere (6×10^9 molec cm⁻³), led to estimated rates of SO₂ oxidation as high as 1.9% hr⁻¹ and the conclusion that the HO₂-SO₂ reaction could be a major source of oxidation of atmospheric SO₂.¹ However recent more direct studies of the HO₂-SO₂ reaction system by Graham et al.²² and Burrows et al.²³ show clearly that these reactions are very slow: $k_{47} + k_{48} \leq 1 \times 10^{-18}$ and $\leq 2 \times 10^{-17}$ cm³ molec⁻¹ sec⁻¹, respectively, were found. It is possible that the expected H₂O₂ product of the reaction, $2HO_2 \rightarrow H_2O_2 + O_2$, in the study of Payne et al.²¹ condensed somewhat with H₂O on the walls of the reactor and oxidized SO₂ at the fast rates characteristic of the solution phase oxidation of HSO₃⁻(aq) by H₂O₂(aq). In any case the interpretation of the latest work seems unambiguous.

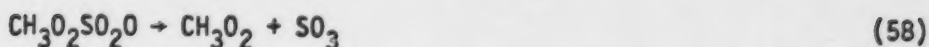
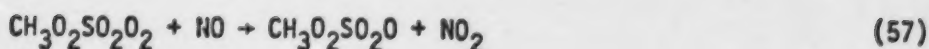
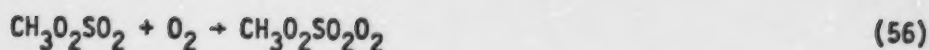
The studies of Burrows et al.²³ involved HO₂-radical detection by laser magnetic resonance in experiments in the 1-5 torr range, and evidence for or against the possible significance of the reaction 48 involving HO₂ addition to SO₂ in the higher pressures of the atmosphere could not be derived from these data. However the studies of Graham et al.²² which involved a HO₂NO₂ thermal source of HO₂ radicals in mixtures of SO₂ at 1 atm pressure, suggests the unimportance of reaction 48 as well as 47. The latest data show that the maximum rate at which SO₂ atmospheric oxidation can occur by 47 and 48 is less than 4.3×10^{-2} to 2.1×10^{-3} % hr⁻¹.

The analogous possible reactions of the alkylperoxy and acylperoxy radicals with SO₂ are somewhat more exothermic than the HO₂-SO₂ reactions, and one might expect these to have somewhat higher rates. This expectation

is not borne out by the data for acetylperoxy and t-butylperoxy radical reaction with SO_2 . Whitbeck et al.²⁴ found that $k_{51} + k_{52} \approx 7 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ at 25°C . Calvert et al.,¹ using data of Pate et al.²⁵ and Hendry and Kenley²⁶ estimated that $k_{53} + k_{54} \approx 1.3 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. Cox and Derwent came to a similar conclusion in kinetic studies of peroxyacetylnitrate-sulfur dioxide mixtures.²⁷ They estimated $k_{53} + k_{54} \approx 7 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. For reasonable concentrations of these peroxy radicals which are anticipated for the urban troposphere ($< 10^8 \text{ molec cm}^{-3}$), the rates of reactions 51-54 cannot be important for SO_2 oxidation ($< 2.5 \times 10^{-5} \text{ hr}^{-1}$).

The data for the CH_3O_2 - SO_2 reactions are less clear. Existing studies point to apparently conflicting conclusions. Whitbeck et al.²⁴ and Kan et al.²⁹ first reported rate data related to this system. They studied the reaction using kinetic flash spectroscopy to follow the CH_3O_2 radical in mixtures with SO_2 , and they derived for experiments at 25°C , $k_{49} + k_{50} = (1.1 \pm 0.2) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. In similar experiments near 25°C , Sanheusa et al.³⁰ found nearly identical results: $k_{49} + k_{50} = (8.2 \pm 0.5) \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. Simonaitis and Heicklen³¹ also determined the competitive rates of CH_3O_2 reactions with NO and SO_2 using steady state photolyses of azomethane- SO_2 - NO - O_2 mixtures. The addition of SO_2 to the azomethane- NO - O_2 mixture increased the quantum yield of NO oxidation, presumably as a result of additional reactions involving CH_3O_2 interactions with SO_2 :

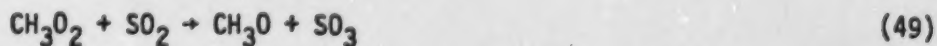


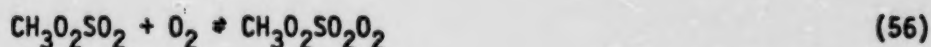
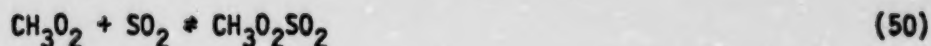


From their relative rate constant estimate, $k_{50}/k_{55} = (2.5 \pm 0.5) \times 10^{-3}$ and an average of current direct estimates of $k_{55} = (6.2 \pm 2.2) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$,³²⁻³⁵ we derive $k_{50} = (1.6 \pm 0.7) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$, in reasonable accord with the more direct estimates.

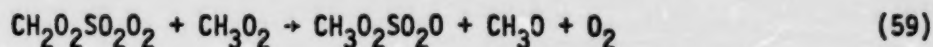
However in subsequent steady state photolyses of azomethane- SO_2 - O_2 mixtures designed to determine the nature of the products of the reactions 49 and 50, Kan et al.³⁶ found little reaction between CH_3O_2 and SO_2 ; their results suggested $k_{49} + k_{50} \leq 1 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$.

Sander and Watson³⁷ also studied the azomethane- O_2 - SO_2 system in flash photolysis studies which were at about one-thousandth of the intensities employed by Kan et al. They found very little reaction between SO_2 and CH_3O_2 and reported $k_{49} + k_{50} \leq 5 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. Kan et al. attempted to resolve these divergent findings in a kinetic flash study at varied flash intensities. They found that the apparent value of $k_{49} + k_{50}$ was dependent on the flash intensity, decreasing to near zero at very low intensities. Their evaluation of the various possible alternative explanations led to the conclusion that reaction of CH_3O_2 with SO_2 did not occur at all through channel 49 and that the reaction 50 and the subsequent reaction 56 with O_2 were reversible:





According to this hypothesis only at high intensities where radical-radical encounters were most favored, did the $\text{CH}_3\text{O}_2\text{SO}_2$ and $\text{CH}_3\text{O}_2\text{SO}_2\text{O}_2$ radicals live long enough to react in 59 (or some similar radical-radical reaction) and hence lock in the oxidized form of SO_2 :



The $\text{CH}_3\text{O}_2\text{SO}_2\text{O}$ radical cannot regenerate SO_2 . This result is also consistent with the findings of Simonaitis and Heicklen.³¹ Even though the CH_3O_2 radical concentrations were low in their experiments, the added NO led to reaction 57 which would also prevent both the decay of the original $\text{CH}_3\text{O}_2\text{SO}_2$ and $\text{CH}_3\text{O}_2\text{SO}_2\text{O}_2$ radicals and the regeneration of SO_2 .

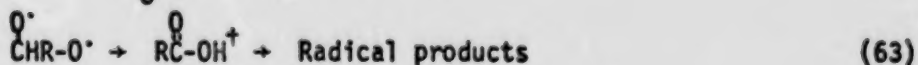
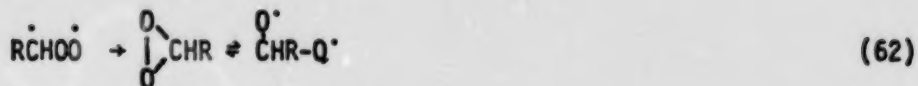
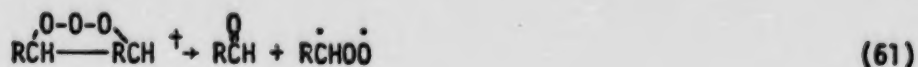
In further steady state experiments with CH_3O_2 , NO_x , SO_2 , O_2 mixtures and Fourier transform spectroscopy for product analysis, Kan et al.³⁶ found that SO_2 did react to form a compound whose absorption peaks were consistent with the structures, $\text{CH}_3\text{O}_2\text{SO}_2\text{ONO}_2$ or $\text{CH}_3\text{O}_2\text{SO}_2\text{O}_2\text{NO}_2$. They concluded that the effective rate of the CH_3O_2 radical oxidation of SO_2 in a polluted atmosphere will be a complex formation of the concentrations of peroxy radicals, NO, NO_2 and conceivably other radical transients which are present. Present data do not allow a quantitative treatment of this reaction system for realistic atmospheric conditions. However in view of the results of Kan et al. it appears reasonable to assume that the CH_3O_2 - SO_2 reaction will be unimportant for SO_2 oxidation in

atmospheric mixtures relatively low in NO, NO₂, and peroxy radical impurities. However for highly polluted atmospheres the effective rate of SO₂ oxidation by CH₃O₂ could become significant, presumably with $k_{50} = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. Obviously further work on this system is required to allow a quantitative consideration of the role of CH₃O₂ radicals in SO₂ atmospheric oxidation. There is no realistic alternative now available to modelers but to use $k_{49} + k_{50} = 0$ in atmospheric simulations, although this practice may result in the underestimation of the importance of the reaction 50 for conditions of high pollution. It would be very surprising if the CH₃O₂-SO₂ reaction results were unique among the alkylperoxy radicals. It is likely that other primary alkylperoxy radicals (C₂H₅O₂, n-C₃H₇O₂, n-C₄H₉O₂, etc.) will behave like CH₃O₂. If the interpretation of Kan et al. is correct these radicals may also play a role in SO₂ atmospheric oxidation. However it is not clear why these primary radicals may react significantly to oxidize SO₂ while the t-butylperoxy and acetylperoxy species do not react under similar conditions. This problem remains unresolved in our minds.

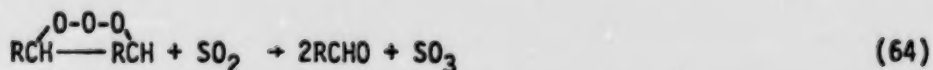
D. The Oxidation of SO₂ by Products of the Alkene-Ozone Reactions

Although the rate of reaction of ozone with SO₂ is extremely slow, the addition of an alkene to a dilute O₃-SO₂ mixture in air results in the significant oxidation of the SO₂.³⁸ Several possible chemical species could be the oxidizing agent here:¹ the ozonide formed in 60; the primary Criegee intermediate formed in 61, the rearranged intermediate formed in 62, or, possibly, the HO- or other radical fragmentation product of the rearrangement and decomposition of the vibrationally-

rich products of the reaction 63.

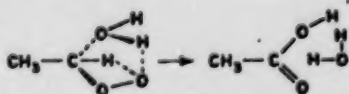


Each of the possible reactants could oxidize SO_2 in the highly exothermic steps 64-66:

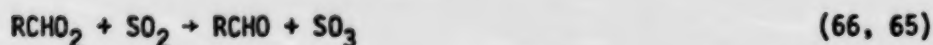


The species $\dot{R}CHOO$ and $\begin{array}{c} O \\ | \\ \text{---} \end{array} RCH-O \cdot$ appear to be the most viable candidates for the reactant with SO_2 here.

Subsequent more detailed studies of the O_3 -alkene- SO_2 -air system by Cox and Penkett³⁹ gave strong kinetic evidence of an inhibition of the SO_2 oxidation by increased H_2O vapor concentration. Calvert et al.¹ speculated that an H_2O - $\dot{R}CHOO$ complex could form and catalyze the rearrangement of the $\dot{R}CHOO$ (or $\begin{array}{c} O \\ | \\ \text{---} \end{array} RCH-O \cdot$) species to the corresponding acid:



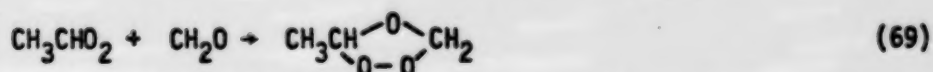
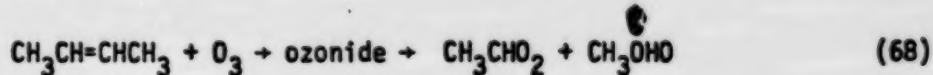
Indeed Hatakeyama et al.⁴⁰ found that the CH_2O_2 species reacted with H_2^{18}O to produce labeled formic acid as expected from this picture. Cox and Penkett's results gave no absolute rate constants, but Calvert et al.¹ have treated their data from *cis*-2-butene reactions in terms of this mechanism and derived the rate constant ratio, $k_{67}/k_{66(65)} = (6.1 \pm 0.3) \times 10^{-5}$.



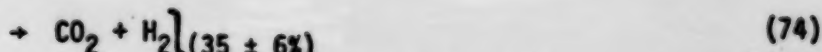
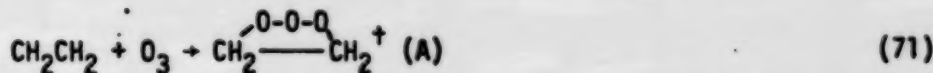
Whether the explanation of the effect given by Calvert et al. is correct or not, the remarkable inhibition of the SO_2 oxidation shown by H_2O is unexpected from species such as HO , HO_2 , and RO_2 whose concentrations are little effected by the presence of H_2O vapor. Thus a maximum of only a few percent of HO_2 radicals are hydrated in the gas phase ($\text{H}_2\text{O}-\text{HO}_2$) at ordinary temperatures and humidities.^{1,41} CH_3O_2 radicals show no evidence of significant hydration as monitored from the insensitivity of the $\text{CH}_3\text{O}_2-\text{CH}_3\text{O}_2$ reaction rate constant to H_2O vapor concentration.⁴² The H_2O effect observed by Cox and Penkett seems to be most reasonably related to the H_2O effect on the Criegee intermediate.

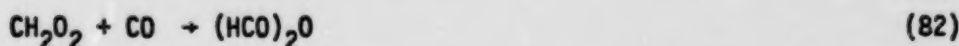
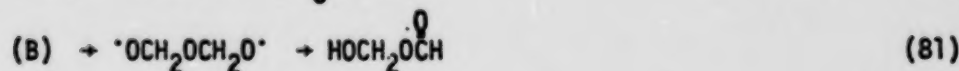
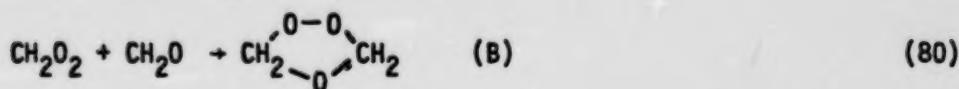
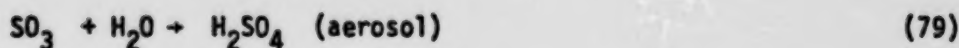
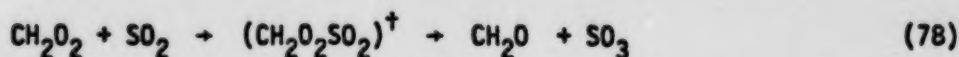
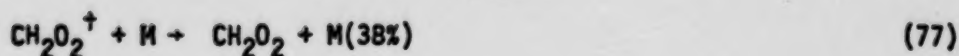
Several experiments demonstrate the reality of the Criegee intermediate in these gas phase O_3 -alkene systems. The identification of the intermediate dioxirane, CH_2O_2 , in the low temperature reaction of ozone and ethylene^{43, 44} provides convincing evidence for the role of Criegee intermediates in these systems. Presumably it arises in reaction 62. Niki et al.⁴⁵ showed clearly that a large fraction of the gas phase ozonolysis of *cis*-2-butene occurs via the Criegee intermediates as well.

In a further study of this system, Niki and his coworkers found new evidence of the nature of the SO_2 reactant in O_3 -alkene- SO_2 systems.⁴⁶ The normal propyleneozonide product formation in cis-2-butene- CH_2O - O_3 mixtures (reaction 69) was quenched with the addition of a small amount of SO_2 , and the SO_2 was consumed (to form aerosol, presumably H_2SO_4) to the extent the ozonide was formed in the absence of SO_2 . Presumably SO_2 in reaction 70 competed favorably with CH_2O in 69 for the CH_3CHO_2 species:



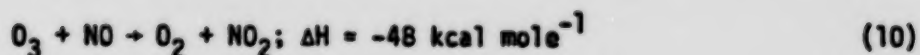
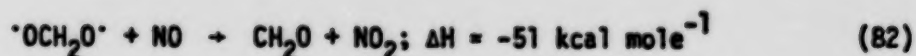
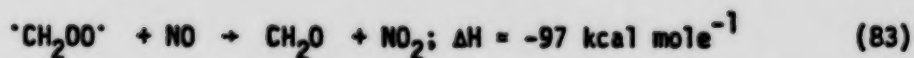
In further recent studies Su et al.⁴⁷ used ppm concentrations of C_2H_4 , O_3 , CH_2O , CO , and SO_2 in N_2 , O_2 mixtures near room temperature and 700 torr total pressure. They determined the relative rates of the reaction intermediate (presumably CH_2O_2) with SO_2 , CH_2O and CO gases. The mechanism for the C_2H_4 - O_3 - SO_2 system suggested by this work and that of the further studies by Kan et al.⁴⁸ and Niki et al.⁴⁹ is as follows:





The fraction of the initial CH_2O_2 species formed in the $\text{O}_3\text{-C}_2\text{H}_4$ reaction in air near 1 atm pressure which is vibrationally relaxed and lives to react by other than decomposition is large: $\sim 38\%$,⁴⁷ $35 \pm 5\%$,⁴⁹ and $37 \pm 2\%$ (independent of temperature, 9-30°C).⁴⁸ The relative rate constants for CH_2O_2 reactions with SO_2 in 78, CH_2O in 80, and CO in 82 are : 400 : 100 : 0.7. It is clear that SO_2 oxidation can occur efficiently through the CH_2O_2 species, and the higher analogues appear to behave similarly. Thus with the higher alkenes Cox and Penkett estimated that about 10% of the intermediate survived reaction with H_2O at $40 \pm 10\%$ relative humidity and could oxidize SO_2 .

Unfortunately it is difficult to assess the significance of the alkene- O_3 reaction products as SO_2 oxidants in the real atmospheres, since one important relative rate constant for the active intermediates is missing. Data for the competitive rates with SO_2 and NO are required. The endothermicities of the possible reactions of CH_2O_2 with NO are equal to or greater than that of the analogous reaction with the structurally and electronically similar compound, ozone:

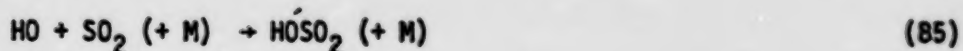


Thus one might anticipate that $k_{83} \approx k_{84} = k_{10} = 1.6 \times 10^{-14} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.⁵⁰ Until reliable kinetic information on the influence of NO on the oxidation of SO₂ by CH₂O₂ and equivalent species is available, the significance of these Criegee intermediates in SO₂ atmospheric reactions must remain speculative. However for relative clean tropospheric air, low in NO, but with levels of the ethene at the ppb level and O₃ near the 0.1 ppm level, the maximum rate of SO₂ oxidation from these O₃-C₂H₄ product reactions is 0.03% hr⁻¹. The presence of the more reactive alkenes at this level lead to rates of SO₂ oxidation of a few tenths of percent hr⁻¹. Since these reactions are not directly dependent on sunlight generation, they will continue unaltered in rate at night, as well as during the day, as long as the alkene and ozone supply is maintained. Further quantitative work on the RHC₂O₂ rate constants with NO and other atmospheric impurities is needed to allow a more quantitative assessment of this possible SO₂ oxidation pathway.

E. The Atmospheric Oxidation of SO₂ by HO-Radicals

It has been recognized for many years that free radicals add to sulfur dioxide to form various transient radical products. For example, H-atoms,⁵¹ various alkyl radicals (CH₃,⁵²⁻⁵⁴ C₂H₅,⁵⁵ CH₂¹⁸FC₂H₂,⁵⁶) cyclohexyl radicals,⁵⁷ and 1,4-biradicals generated from quinone-alkene-

SO₂ mixtures,^{58,59} all add readily to SO₂. The rate constant for these reactions are large, near those for free radical reactions with O₂. In light of these data it is not surprising that the hydroxyl radical (HO) adds readily to SO₂ as well.



McAndrews and Wheeler⁶⁰ were apparently among the first researchers to suggest the importance of this reaction. They used it to rationalize the effect of SO₂ on radical chain termination in propane-air flames. Following the suggestions of Fair and Thrush,⁶¹ one can use the McAndrew and Wheeler rate data to estimate the approximate third order rate constant, $k_{85} = 1.1 \times 10^{-31} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$ at 2080 K.

It is now generally accepted by atmospheric scientists that the reaction 85, the addition of HO-radicals to SO₂, is the major rate controlling step in the gas phase oxidation of SO₂ in the troposphere. For this reason we should consider here in some detail the best current evidence which bears on this conclusion and derive from the present data the "best" estimates for the rate constants for this reaction at atmospheric conditions. We will examine carefully the methods of measurement, the assumptions necessary to derive the rate constant estimates, and the probable reliability of the existing data.

1. The Elementary Rate Constant for HO Addition to SO₂

The HO-SO₂ reaction 85 is kinetically in the third order region at gas pressures below a few torr; that is, the rate of SO₂ reaction in 85 is proportional to the product of three concentration terms:

$$-d[SO_2]/dt = [HO][SO_2][M]k_{III}(85).$$

Reaction 85 is in the transition region between third and second order kinetics in the pressure region characteristic of the troposphere; the rate become less sensitive to the concentration of the third body M as the pressure increases. Even at the highest pressures of the lower atmosphere the measured value of the apparant second order rate constant has not yet reached its pressure independent value characteristic of the high pressure limit. For measurements made at a constant pressure it is convenient to describe the rate of reaction 85 in terms of an apparent second order constant:

$$-d(SO_2)/dt = [HO][SO_2]k_{II}(85).$$

The dependence of $k_{II}(85)$ on $[M]$ in the pressure range characteristic of the troposphere is a complex function of k_{III} , $k_{II}(85)$ at infinite pressure, and $[M]$; see equation 124 of section VI. As we shall see, this dependence on the pressure and nature of the third body M complicates the determination of useful k_{85} data applicable to the atmosphere.

Measurements of the rate constant for the elementary reaction through the direct detection of the HO-radicals have been made in several laboratories in recent years. In principle these data should be the most reliable available. The relative HO-radical concentration was monitored through resonance fluorescence detection, and the reaction was studied under conditions of pseudo first order conditions; that is, an excess of SO_2 reactant was used so that its concentration was essentially constant in a given experiment. The HO-radicals, formed in a flash photolysis of

H₂O, through the $H + NO_2 \rightarrow HO + NO$ reaction in a flow system, or by other means, were followed as a function of time through their emission of resonance fluorescence which was excited in a small fraction of the HO population present in the reacting mixture. The fluorescence intensity $(I_f)_t$ at any given time (t) is directly proportional to the [HO] at that time. For these conditions the integrated rate law for the intensity as a function of time is given by 86:

$$\ln (I_f)_t = k_{II(85)}[SO_2]t + C \quad (86)$$

where C is a constant. The slope of a plot of $\ln (I_f)_t$ versus time gives $k_{II(85)}[SO_2]$; since $[SO_2]$ is constant and known for each experiment, $k_{II(85)}$ can be calculated. This is the apparent second order rate constant for reaction 85; unfortunately this directly measured quantity it is not the value of $k_{II(85)}$ which we require for use in atmospheric studies of reaction 85 because of the peculiar composition of the reaction mixtures necessary either to generate the HO-radicals or to carry them along in the reaction tube of the flow system. The reaction mixture cannot be the relatively pure air characteristic of the troposphere. The effective efficiency of the components of this mixture as stabilizing collision partners (M) for the initial HOSO₂ radical product of reaction 85 will be different for each gas--more efficient for complex M molecules, less efficient for the simple M molecules. For example, Leu has determined in a series of experiments with varied reactant and added gas composition that the relative efficiencies of He, N₂, O₂, SO₂, and CO₂ as M in reaction 85 are in the ratio: 1.0: 4.0: 3.9: 16.6: 19.3, respectively. Once these ratios have been determined carefully, which

is no routine task, then the effects of the various gases necessarily present in the reaction mixture (SO_2 , H_2O , He, or other) can be factored out, and the influence due to the atmospheric gases N_2 or O_2 alone as M can be derived. The process of separation of the rate constants into the components from each type of M is probably the largest source of the differences in $k_{\text{II}}(85)$ values reported by the different workers.

At sufficiently low pressures where reaction 85 is in the third order region, values of $k_{\text{II}}(85)$ are directly proportional to $[\text{M}]$; $k_{\text{II}} = [\text{M}]k_{\text{III}}$, where k_{III} is the true third order rate constant. The first measurements of $k_{\text{III}}(85)$ with N_2 as M were made by Harris and Wayne⁶¹; see Fig. 2 (open triangles), Davis et al.⁶² (diamonds in Fig. 2), and very recently by Leu (squares in Fig. 2).⁶³ The data from the different laboratories show little consistency with one another, and this is understandable in terms of the potential problems we have considered which make these measurements non-trivial in nature. The recent work of Leu is the most extensive study, and his results seem to offer the best estimates of $k_{\text{III}}(85)$ for $\text{M} = \text{N}_2$. A unique, very important observation was made by Leu. He also studied reaction 85 with $\text{M} = \text{O}_2$. His data for $k_{\text{II}}(85)$ ($= k_{\text{III}}(85)[\text{M}]$) with $\text{M} = \text{N}_2$ and $\text{M} = \text{O}_2$ are compared in Figure 3. Obviously these gases have about the same efficiency as M in reaction 85, a fact which we will require in deriving our best estimates of the high pressure values of $k_{\text{II}}(85)$.

There are serious problems in measuring $k_{\text{II}}(85)$ at tropospheric pressures of air, the very conditions which are most important for the input of reaction 85 to acid rain development in the troposphere. Unfortunately accurate experiments with the direct detection of HO-

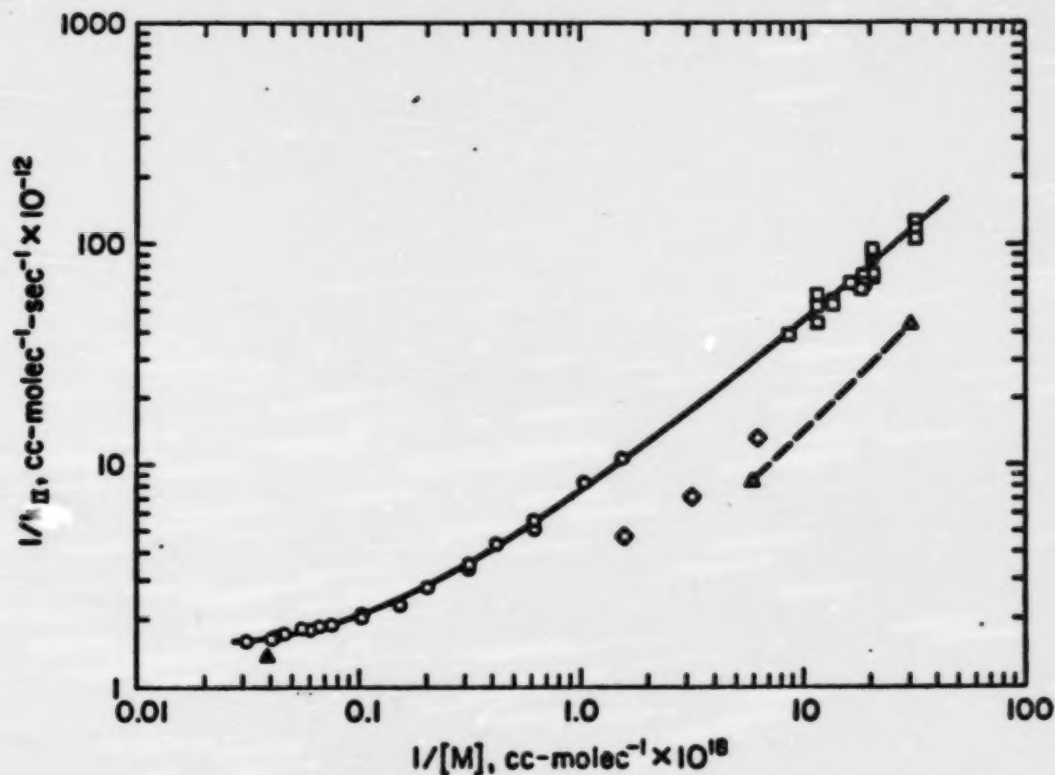


Figure 2. Comparison of the experimental data for the effective second order rate constants for the reaction $\text{HO} + \text{SO}_2 (+\text{M}) \rightarrow \text{HOSO}_2 (+\text{M})$ with $\text{M} = \text{N}_2$; corrected data of Castleman and Tang⁶⁴ (circles); Leu (squares)⁶³; Harris and Wayne (triangles show the range of values reported);⁶¹ Davis et al. (diamonds)⁶²; Cox and Sheppard (filled triangle)⁶⁶.

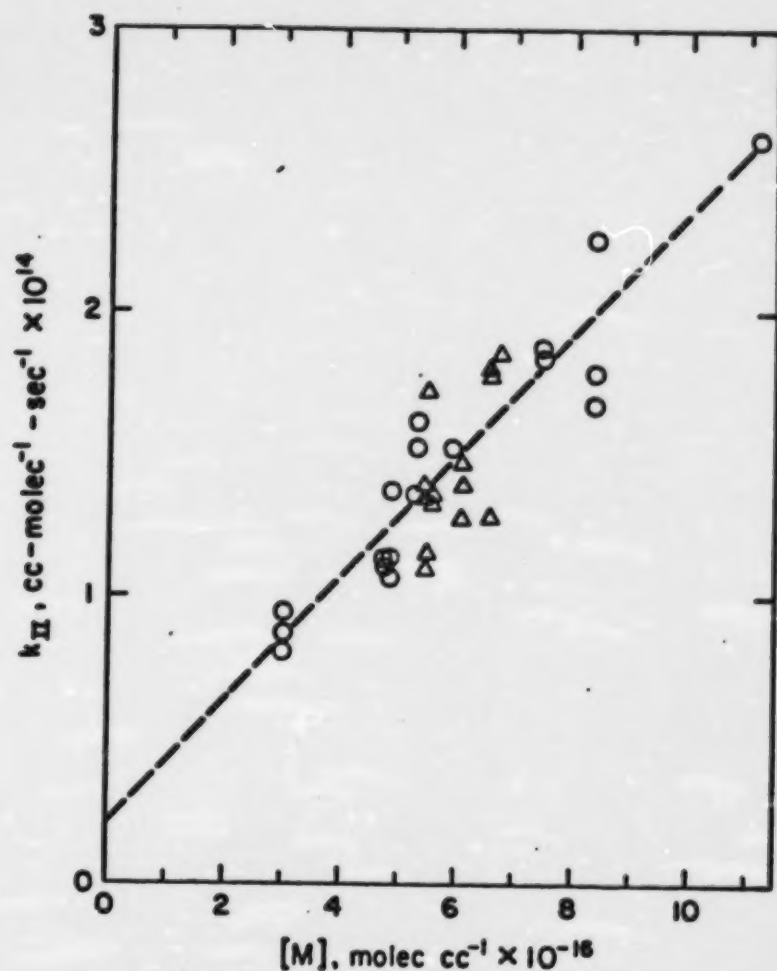
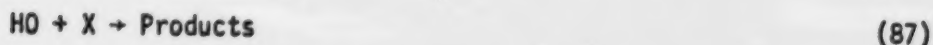


Figure 3. Apparent second order rate constants from Leu⁶³ for the reaction 85, $\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$, at low pressures; $\text{M} = \text{N}_2$ (circles); $\text{M} = \text{O}_2$ (triangles).

radicals in mixtures at 1 atm of air have been impossible to date. The quenching of excited HO-radicals by nitrogen and oxygen gases is very effective and limits the usefulness of this direct method of $k_{II(85)}$ determination. The only information which we have on the kinetics of reaction 85 at high pressures of nitrogen or air was derived from competitive rate studies, and we must use these data until more direct methods have been developed.

The competitive rate studies of HO-reaction with SO_2 are simple in theory. A source of HO radicals is mixed with a dilute mixture of SO_2 and some reference compound X for which the absolute rate constant for reaction with HO is well known. The HO-radicals react in 85 and 87 to remove SO_2 and X:



If there is no significant reaction of the product $HOSO_2$ of 85 and those of 87 with SO_2 or X, then the following rate laws apply:

$$-\frac{d[SO_2]}{dt} = [SO_2][HO]k_{II(85)} \quad (88)$$

$$-\frac{d[X]}{dt} = [X][HO]k_{87} \quad (89)$$

Of course the $[HO]$ in the mixture is common to both reactants at a given time, and in taking the ratio of 88 and 89 this unknown quantity cancels out. Thus the ratio of rate constants is related to the measured rates and concentrations simply by relation 90:

$$\frac{k_{11(85)}}{k_{87}} = \frac{\frac{d[SO_2]}{dt} \frac{1}{[SO_2]}}{\frac{d[X]}{dt} \frac{1}{[X]}} \quad (90)$$

Thus if we measure the concentrations of SO_2 and X as a function of time, then the term on the right of equation 90 is easily evaluated, and from the known value of k_{87} we may derive $k_{11(85)}$.

In the published studies using this method of $k_{11(85)}$ estimation, Castleman and Tang⁶⁴ used CO as the reference gas X ; Cox⁶⁵ employed NO and NO_2 (based ultimately on CO) as X , while Cox and Sheppard took C_2H_4 as X .⁶⁶ However only in the latter study was the rate of SO_2 loss followed directly. In the other two studies the perturbations produced in the X loss rate were noted on the addition of SO_2 to the reaction mixture. The rate of the HO-radical- SO_2 reaction was inferred from this and an assumed mechanism. The correctness of this procedure depends upon an accurate knowledge of the complete mechanism; in particule the fate of the $HOSO_2$ radical must be known. Does it react with additional HO-radicals? Does it regenerate HO-radicals in subsequent steps in the mechanism? Does it react with X ? Since the subsequent reactions of the $HOSO_2$ initial product of 85 are ill-defined today (See the discussion of the following section.), relative rate measurements to derive estimates of the $k_{11(85)}$ do not offer unabmiguous results in most cases. However the seeming uniqueness and correctness of the k_{85} values measured by the more direct experiments in which the $[HO]$ is monitored, also suffer from many of the same problems. Thus we must know the fate of the $HOSO_2$ species in this case to define its potential reaction with HO-radicals in subsequent steps if we are to eventually relate the

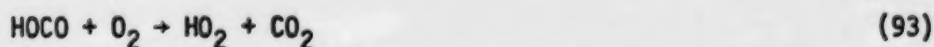
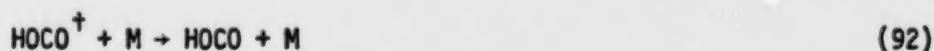
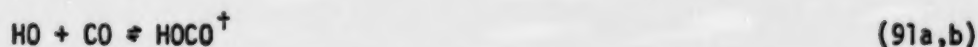
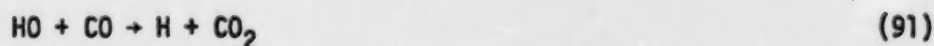
measured HO loss rates to reaction 85. This problem, inherent with reactions forming initial radical products, is not present for reaction systems such as $\text{HO} + \text{NO}_2 (+ \text{M}) \rightarrow \text{HONO}_2 (+ \text{M})$, or other reactions producing relatively stable molecules. The concern expressed here that possible problems exist in the direct as well as the indirect measurements of $k_{\text{II}(85)}$, is not academic. Leu has observed that the decay of HO in $\text{SO}_2\text{-O}_2$ mixtures deviates from the expected first order decay at long observation times; indeed it seems that reformation of HO-radicals occurs in some undefined subsequent reaction step involving the initial product of 85. Leu corrected for this problem by taking initial rate data. The point which we wish to emphasize here is that any rate measurement of reaction 85, be it direct or indirect, has serious potential problems associated with it, and the inherent errors in estimates of k_{85} may be large. Certainly our use here of competitive rate constant data does not open a Pandora's Box full of new problems. These are a few special problems with the high pressure work, however, which we must consider.

In the case of both the competitive studies of Cox⁶⁵ and Castleman and Tang⁶⁴ the HO-CO reaction was chosen as the reference reaction.



Since these studies were made it has been shown that reaction 91 has an unexpected, marked pressure dependence of the apparent second order rate constant, k_{91} ,⁶⁷⁻⁷² and hence the estimates for k_{85} reported by these workers and based on k_{91} must be corrected. The studies of Biermann et al.⁷² give the clearest picture of the effect of nitrogen and oxygen on

k_{91} . Basically they showed that provided a trace of oxygen was present in their gas mixtures (greater than 0.25 torr) the rate constant k_{91} increased linearly with N_2 pressure; see Figure 4. With very highly purified N_2 or other added gases the pressure dependence was absent. These unusual results were rationalized in terms of a second, pressure sensitive, reaction channel for reaction 91 in which a complex ($HOCO^\dagger$) of finite lifetime was involved. Presumably this complex could be stabilized by a colliding partner, and in the presence of small amounts of oxygen, it could react to form HO_2 and CO_2 :



The k_{91} data of Biermann et al. from experiments at different N_2 pressures ($P_{O_2} > 0.25$ torr) are plotted in Fig. 4 (circles). Also shown as squares are the data of Chan et al. for synthetic air mixtures.⁶⁹ The least squares fit of the Biermann et al. data at 300 K give $k_{91} = (1.32 \pm 0.06) \times 10^{-13} + (1.76 \pm 0.11) \times 10^{-16} P_{N_2}$ (torr). The first term which corresponds to the second order component of reaction 91 agrees well with the results for k_{91} from previous low pressure experiments: $(1.48 \pm 0.15) \times 10^{-13}$,⁷³ 1.35×10^{-13} ,⁷⁴ 1.33×10^{-13} ,⁷⁵ 1.44×10^{-13} ,⁷⁶ 1.33×10^{-13} ,⁷⁷ $(1.54 \pm 0.16) \times 10^{-13}$,⁷⁸ 1.7×10^{-13} .⁷¹ The oxygen content of the nitrogen gas used by Castelman and Tang is not

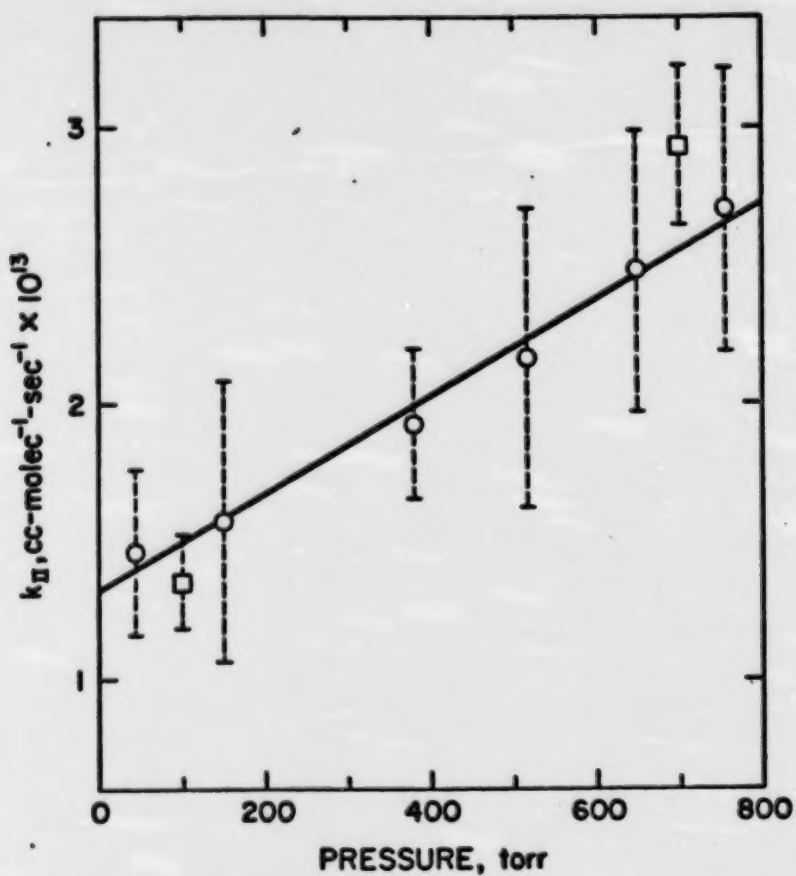
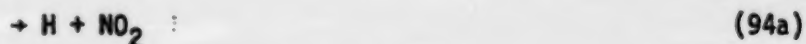


Figure 4. Plot of the apparent second order rate constant for reaction 91, $\text{HO} + \text{CO} (+\text{M}) \rightarrow \text{H} + \text{CO}_2 (+\text{M})$, as a function of N_2 pressure ($P_{\text{O}_2} \approx 0.25$ torr) from experiments of Biermann et al. (circles);⁷² air pressure varied in the studies of Chan et al. (squares).⁶⁹

known, but O_2 -free, purified N_2 gas was not employed.⁷⁹ Thus our previous experience suggests that it is highly probable that the pressure sensitive component of the reaction 91 was operative here, and corrections to their results for $k_{II(85)}$ are required. The data so corrected are plotted as open circles in Figure 2. It can be seen that these results seem to mesh well with those reported recently by Leu from experiments at low pressures. Since O_2 and N_2 are equally effective as M within the error of Leu's measurements (See Figure 4.), the results of Castleman and Tang and Leu can be combined to provide the $k_{II(85)}$ values for 25°C and the range of pressure of the troposphere. We will use this set of data as the most reliable source of rate information related to $k_{II(85)}$. Other related, but not directly applicable, published data for $k_{II(85)}$ appear to be consistent with the results we have chosen to use here. Thus the pressure dependence of the $k_{II(85)}$ as observed by Atkinson et al.⁸⁰ is in reasonable accord; they used M = Ar and M = SF_6 at pressures up to 650 torr. They suggest $k_{II(85)} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ for M = N_2/O_2 at 760 torr and 25°C; this was based upon a reasonable extrapolation of their data and the relative efficiencies of N_2 , O_2 , Ar, and SF_6 for the similar association reaction, $HO + NO_2 (+M) \rightarrow HONO_2 (+M)$. Our treatment of the Castleman and Tang data gives $k_{II(85)} = 1.14 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ for 760 torr of air at 25°C.

The early results of Cox⁶⁴ based upon the photolysis of dilute mixtures of HONO, HO, NO_2 , SO_2 and HONO, NO, NO_2 , CO in air also agree within the large experimental error when corrected for the pressure effect on the reference reaction 91. His preferred method of treatment

of the data gives $k_{11}(85) = (1.1 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ for 760 torr of air at 25°C. However there are several special problems related to the interpretation of these results. First there is evidence of an unknown HO-reactive impurity in the mixtures which Cox employed. NO_2 was generated on photolysis of the "pure" HONO- NO_x mixtures in air. Cox first attributed this to the occurrence of primary process 94a in HONO photolysis in addition to the commonly accepted process 94:

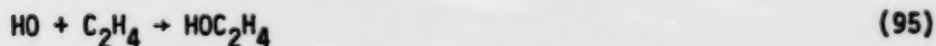


We find this process to be unimportant, and in later experiments of Cox the same judgement was made.⁸² Cox's rate data can be simulated well with 94 as the only primary photochemical process in HONO photolysis but with CO or hydrocarbon impurities (X) present in his mixture such that $k_x[X] = (4 \pm 2) \times 10^2 \text{ sec}^{-1}$; k_x is the rate constant for HO attack on the X species. A few ppm of reactive impurity (not uncommon in the use of Tedlar bags), can lead to significant HO_2 development and subsequent formation of NO_2 ($\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$) to account for the anomalous NO_2 generation originally attributed to 94a. Cox found some interesting results which do add significantly to our knowledge of the HO- SO_2 reaction. He observed that in experiments at high SO_2 levels, NO was destroyed more rapidly than it was formed by photolysis in 94.[†] In order for more NO to be lost than is made in his experiments, requires

[†]See Figure 2, ref. 65; the minus sign was inadvertently omitted on R_{NO} for run 1-6 in Table I of this reference.

a reaction such as $\text{HOSO}_2\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HOSO}_2\text{O}$ plus some other reaction involving NO loss; e.g., $\text{HOSO}_2\text{O} + \text{NO} \rightarrow \text{HOSO}_2\text{ONO}$. However if this mechanism choice is made Cox's data give a value of $k_{11(85)}$ which is a factor of 0.53 lower than that derived from the chosen mechanism. The favored mechanism involved the decomposition of the HOSO_2O_2 radical ($\text{HOSO}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$); Benson's thermal data⁹¹ show this to be exothermic by 22 kcal mole⁻¹, and thus it is unlikely to be important here. The uncertainties in the complete reaction mechanism operative in Cox's experiment and the high sensitivity of the estimate of the desired rate constant $k_{11(85)}$ to the mechanism choice, does not allow any great weight to be placed on these data. However the $k_{11(85)}$ estimate derived is not inconsistent with our preferred values.

The single data point shown as a closed triangle in Figure 2 was obtained by Cox and Sheppard using competitive rate studies in HONO photolyses in dilute SO_2 , C_2H_4 mixtures in air. Here the actual rates of SO_2 and C_2H_4 loss were measured, and the ratio of $k_{11(85)}/k_{95} = 0.09 \pm 0.02$ was calculated.



Taking $k_{95} = 8 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ they estimated $k_{11(85)} = (0.72 \pm 0.16) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ (760 torr air, 25°C), a value significantly lower than that estimated here from the Castleman and Tang data ($1.14 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$). We feel that there is a potential problem in the use of an alkene as a reference reactant here which

may have led to a low estimate. We have found in previous experiments with SO_2 -azomethane photolysis that CH_3SO_2 radicals add readily to the double bond of azomethane to form an aerosol.⁵³ A similar reaction is expected involving the HOSO_2 , HOSO_2O_2 , or HOSO_2O radicals with C_2H_4 . If one assumes that such a reaction occurs here it is possible to match well the observed, "apparent" rate constant ratio ($k_{11(85)}/k_{95}$) using our estimate of $k_{11(85)}$ and a relative rate constant ratio of about 2 for the reaction of HOSO_2O radicals to add to C_2H_4 and that to abstract H-atoms from HONO . In this case a more rapid rate of C_2H_4 removal than that from HO-attack in C_2H_4 results, and an apparent decrease in the HO- SO_2 rate constant is expected if such a reaction is neglected in the data treatment. In any case further experiments of HOSO_2O , HOSO_2 , or HOSO_2O_2 radical addition to C_2H_4 in this system are required before accepting this seemingly unusual value for $k_{11(85)}$.

From this rather detailed discussion of the current data related to $k_{11(85)}$ the reader should conclude that major uncertainties still remain in our knowledge of this constant, particularly for the important high pressure regime of the troposphere. Our judgement is that the corrected results of Castleman and Tang and those of Leu constitute the best available data today for our use in atmospheric applications. The least squares, quadratic equation fit of these data for $k_{11(85)}$ at 25°C for the various pressure regimes in the atmosphere are summarized in Table III.

The temperature dependence of the HO- SO_2 rate constant has been estimated by several workers. There is general accord that the apparent activation energy of this reaction is negative in agreement with that

Table III. Recommended Relations for $k_{II}(85)$ for Use in Tropospheric Modeling at Various Temperatures and Concentrations of Air^a

1) Pressure Range 500-1000 torr, temperature 298 K:

$$1/k_{II}(85) = 2.433 \times 10^{10} + 2.725 \times 10^{31}(1/[M]) - 1.479 \times 10^{50}(1/[M])^2$$

2) Pressure range 20-500 torr, temperature 298 K:

$$1/k_{II}(85) = 6.035 \times 10^{11} + 8.651 \times 10^{30}(1/[M]) - 1.235 \times 10^{48}(1/[M])^2$$

3) Pressure Range 5-20 torr, temperature 298 K:

$$1/k_{II}(85) = 1.492 \times 10^{12} + 4.564 \times 10^{30}(1/[M]) - 3.403 \times 10^{46}(1/[M])^2$$

(4) Pressure range 0-5 torr, temperature 298 K:

$$1/k_{II}(85) = (1/[M])(3.97 \times 10^{30})$$

(5) Adjustment of $k_{II}(85)$ values derived from the above equations for temperature 298 K to a new temperature T (K):

$$k_{II}(85) \text{ at } T \text{ (K)} = (k_{II} \text{ at } 298 \text{ K})(0.0342) e^{1007/T}$$

^a[M] is the concentration of air in molec cm⁻³; values of $k_{II}(85)$ are in units of cm³ molec⁻¹ sec⁻¹.

observed for other radical-radical and radical-molecule association reactions involving simple species. Castleman and Tang⁶⁴ carried out a low pressure (20 torr) study over a small temperature range (-20 to 24°C) and estimated $E_{85} = -2.8 \text{ kcal mole}^{-1}$. Harris et al.⁸¹ did a more extensive study (298-424 K) at higher pressures (~ 650 torr) using either Ar or SF₆ as M. They found $E_{85} = -1.5 \pm 0.3$ and $-2.4 \pm 0.3 \text{ kcal mole}^{-1}$, respectively, in the two sets of experiments. From these results and considerations of the relative efficiencies of Ar, N₂, O₂, and SF₆ as M in other similar reactions, they estimated that $E_{85} = -1.9 \text{ kcal mole}$ for $k_{II(85)}$ in air at 1 atm. Moortgat and Junge⁸⁵ quote an unpublished estimate of $E_{85} = -2.0 \text{ kcal mole}^{-1}$ by Erler et al.⁸⁴ based on their measurements at 220 and 298 K and low pressures of added gases. In view of the data at hand we feel a choice of $E_{85} = -2.0 \text{ kcal mole}^{-1}$ is a reasonable one for the pressure and temperatures encountered within the troposphere. Estimates of $k_{II(85)}$ for 298 K derived from the appropriate equation 1, 2, 3, or 4 of Table III for the required [M] can be corrected to the desired temperature using the relation 5 of this table. Following this procedure we have made estimates for $k_{II(85)}$ for various altitudes with characteristic pressures, and temperatures defined for the standard atmosphere.⁸⁶ These are shown in Figure 5.

The initial jump in $k_{II(85)}$ seen at 1 km in Figure 5 reflects the relative insensitivity of the $k_{II(85)}$ value to change in pressure in the high pressure regime, but its much stronger sensitivity to the decrease in temperature. The gradual increase in $k_{II(85)}$ up to 11 km is controlled by the decreasing temperature; see the lower graph of temperature versus altitude in Figure 5. As the temperature stabilizes and then falls at

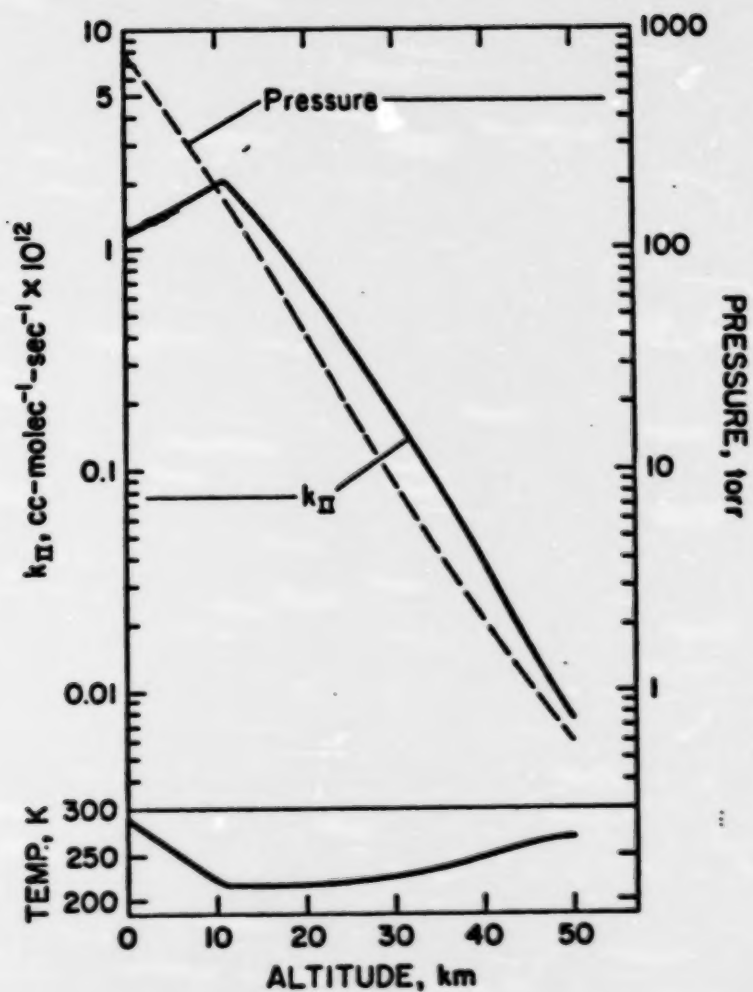


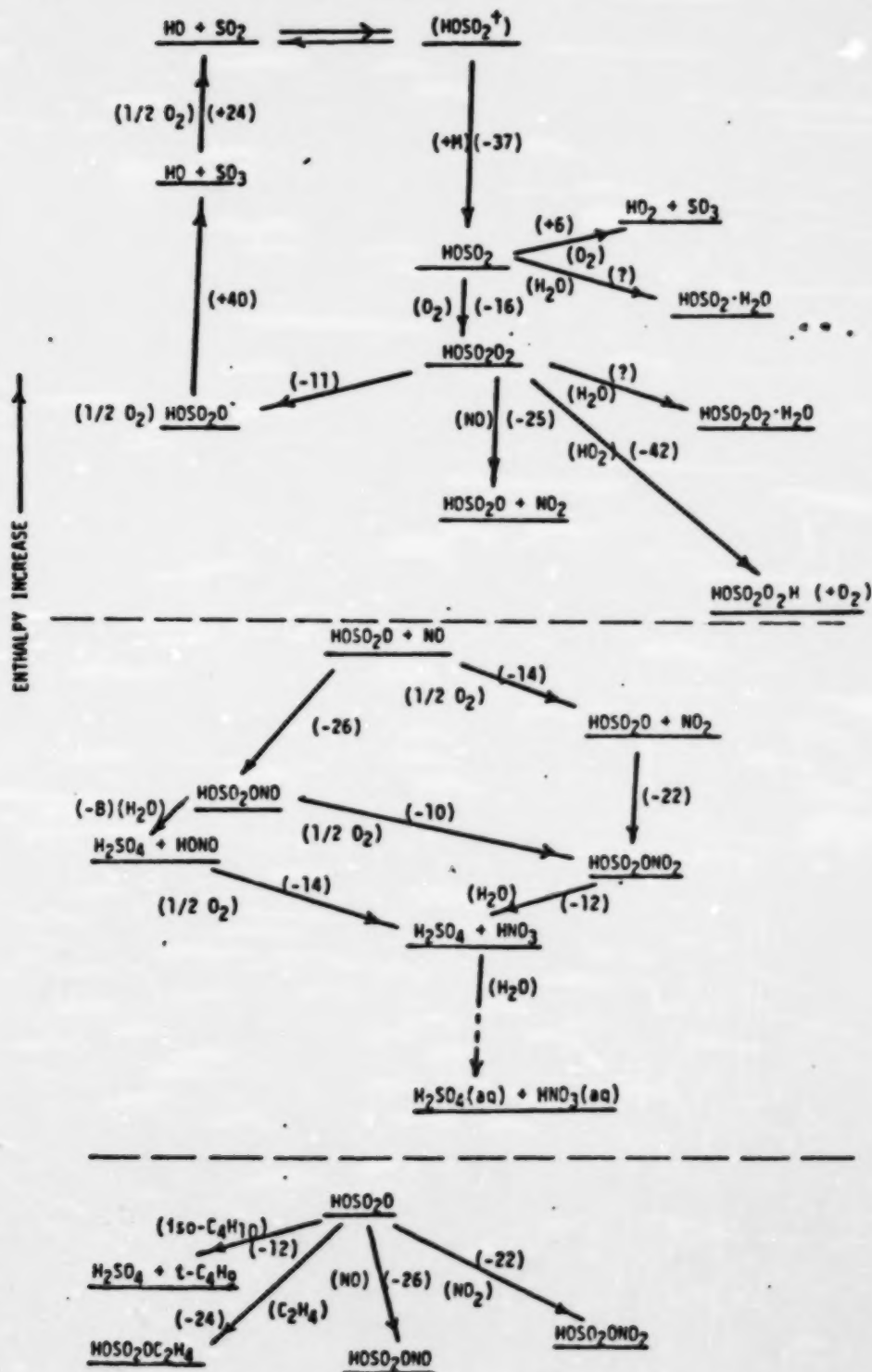
Figure 5. Variation of the apparent second order rate constant for the reaction 85 as a function of altitude; calculated from the equations of Table III for the conditions of pressure and temperature defined for the standard atmosphere;⁸⁶ the pressure is shown as the dashed line; the temperature is shown on the lower part of the curve.

elevations above 11 km, the effective second-order rate constant falls continuously, reflecting both the increased sensitivity to the decreasing pressures and the rising temperatures in this region of the atmosphere. The "best" values of $k_{11}(85)$ suggested from the analysis given here are somewhat larger than those chosen by Moortgat and Junge,⁸³ Zellner,⁸⁵ and the values recommended for use by the CODATA group⁸⁷ and the NASA Panel.⁸⁸ We feel that our choices are more consistent with the information related to the HO-SO₂ reaction which is available at this time. One must, however, retain considerable pessimism about the accuracy of all of these data. We feel that realistic confidence limits should include $\pm 50\%$ of the chosen value at this time. . . .

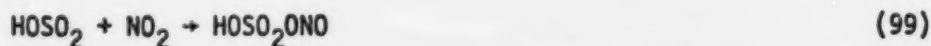
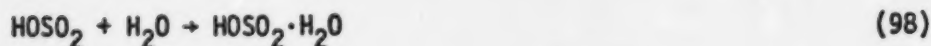
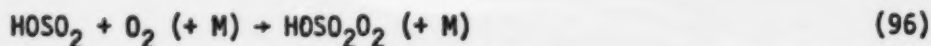
11. The Secondary Reaction of the HOSO₂ Species

There appears to be good evidence that HOSO₂ species formed in reaction 85 ultimately leads to the generation of sulfuric acid aerosol. However HOSO₂ is a free radical which is probably highly reactive toward several atmospheric compounds, and it is not now clear what elementary reaction pathways are important in its conversion to H₂SO₄. Although a great amount of speculation has been given in this regard, there is little experimental evidence to help sort out the suggested alternative routes. Thus Cox,^{65,82} Calvert and McQuigg⁸⁹, Calvert et al.¹, Davis et al.⁶², Friend et al.⁹⁰, Leu⁶³, Benson⁹¹, and others have suggested that the HOSO₂ radical may react in a variety of radical-radical and radical-molecule reactions. These are summarized in Table IV. The initial fate of the HOSO₂ radical in air is generally believed to be an association with O₂ in reaction 96. The exothermicity of this reaction ($\Delta H = -16$ kcal mole⁻¹) and the prevalence of oxygen among the atmospheric gases

Table IV. Enthalpy Relationships between Various Possible Products of the HO-Radical Reaction with SO₂



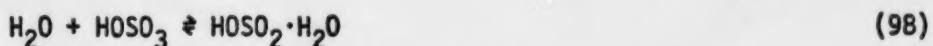
favor this pathway. The alternative disproportionation with O_2 (reaction 97), the direct reaction with H_2O (reaction 98) or impurity molecules such as NO_2 (reaction 99) may also occur, but these appear to be less probable to the present authors:



If the thermochemical estimates of Benson⁹¹ are near correct then reaction 97 is endothermic by about 6 kcal mole⁻¹, and the activation energy is probably much greater. The chance that $HOSO_2$ encounters with impurity levels of NO_2 in 99 will lead to nitrosylsulfuric acid before reaction with O_2 could occur seems small even in highly polluted atmospheres; however reaction 99 is highly favored thermochemically ($\Delta H = -37$ kcal mole⁻¹).

The reaction 98, the association of $HOSO_2$ radicals with H_2O , was suggested by Friend et al.⁹⁰ to rationalize their observed rates of aerosol nucleation in the SO_2 oxidation by HO-radicals. Although this postulate may be correct, there are viable alternatives to explain their results. Presumably a major point in favor of the importance of 98 is that the structure of the $HOSO_2$ radical is very much like that of SO_3 which exhibits a marked tendency to complex and/or react rapidly with H_2O .⁹²⁻⁹⁴ There is little direct evidence to support the contention often made that free radical- H_2O complexes are important. The HO_2

radical forms a complex with H_2O , but only a few percent of the radicals exist in the complex even at high relative humidities.¹ The large entropy decrease which accompanies the association of the radical and water molecules must be overcome by a significant energy release or the complex will be unimportant. We may illustrate this point using reasonable estimates of the thermodynamic quantities associated with 98:



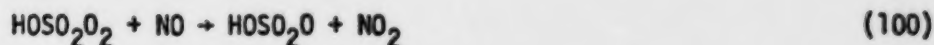
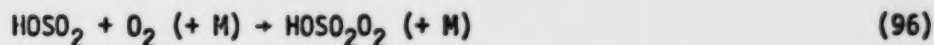
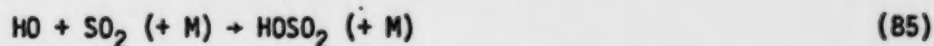
If at 298 K $\Delta H_{98} = -12 \text{ kcal mole}^{-1}$ while $\Delta S_{98}^\circ = -37.3 \text{ ev}$ (1 atm standard state)[†], then at 50% relative humidity and 298 K the ratio of the concen-

[†]This ΔH° estimate was taken as one-half the enthalpy change for the reaction $H_2O + SO_3 \rightarrow H_2SO_4$; the ΔS° was taken as equal to that for this same reaction.

tration of the $HOSO_2 \cdot H_2O$ complex to that for the uncomplexed $HOSO_2$ radical at equilibrium would be only $\sim 4 \times 10^{-3}$. However the stability of the complex is very sensitive to the magnitude of ΔH_{98}° . For example, if $\Delta H_x \sim -16.3 \text{ kcal mole}^{-1}$, then the ratio of complex to uncomplexed radical at equilibrium would be 100 to 1 at 50% relative humidity and 298 K. It seems unlikely to us that the $\Delta H_{98} < -12 \text{ kcal mole}$, and we favor the association of $HOSO_2$ with O_2 in reaction 96 as the dominant fate of this species in the troposphere.

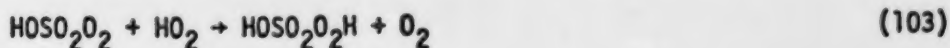
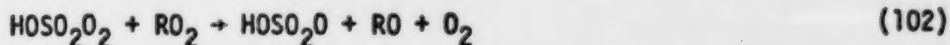
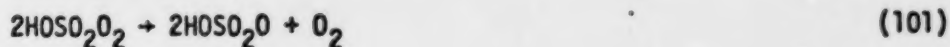
Indeed there is good evidence that the peroxyradical, $HOSO_2O_2$, is formed following the $HO-SO_2$ reaction in air. Thus the addition of SO_2 during the photooxidation of hydrocarbon- NO_x mixtures does not alter significantly the ozone level reached although SO_2 is oxidized.⁹⁵ This

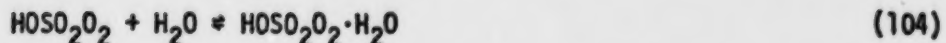
indicates that the removal of an HO-radical by SO_2 in reaction 85 instead of its reaction with a hydrocarbon molecule does not interrupt the chain process of NO to NO_2 conversion. The ultimate level of ozone reached depends on the $[\text{NO}_2]/[\text{NO}]$ ratio. Thus reaction 85 followed by 96 and 100 would fit these observations:



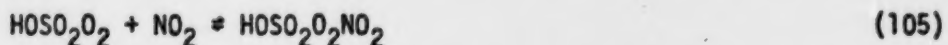
Also as we noted previously Cox⁶⁵ found in $\text{HONO-SO}_2\text{-NO}_x\text{-O}_2$ mixture photolyses that at high SO_2 levels the NO in the mixture was converted faster to NO_2 and possibly other products, than it was formed in the photolysis of HONO. The rapid occurrence of reaction 100 appears to be an important step in the mechanism required to match these observations.

Several pathways for the decay of the HOSO_2O_2 radical, in addition to NO oxidation, are expected in theory. It may react in NO-poor mixtures with other peroxy radicals. Thus it may disproportionate in the fashion observed for alkyl peroxy radicals, or conceivably it could complex with H_2O :

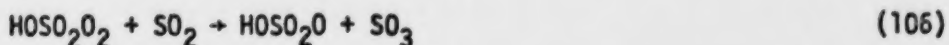




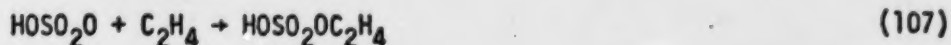
Davis et al.⁶² favor this latter alternative, but as with the suggested hydration of the HOSO_2 radical discussed previously, the evidence for this is not overwhelming. Reaction 101 and 102 as well as 100 form the HOSO_2O radical from HOSO_2O_2 . In 103 the monoperoxysulfuric acid (Caro's acid) is a product. Benson anticipates that the possible product of HOSO_2O_2 with NO_2 in reaction 105 ($\text{HOSO}_2\text{OONO}_2$) would have a very short lifetime. It would be the inorganic analogue to peroxyacyl nitrate (PAN), one of the notorious products common to photochemical smog.⁸⁹

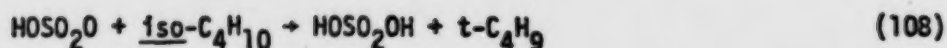


The possible oxidation of SO_2 by HOSO_2O_2 radicals (reaction 106) seems unlikely although $\Delta H_{106} = -35 \text{ kcal mole}^{-1}$; the analogous reactions of near equal exothermicity which involve the acetylperoxy and tert-butylperoxy radicals with SO_2 (53, 51, respectively) are too slow kinetically to be measureable at 25°C .

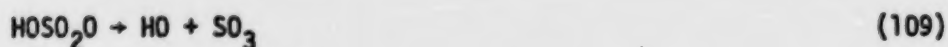


From thermochemical considerations Benson expects the HOSO_2O radical product of many of the HOSO_2O_2 radical reactions to be more active than alkoxy radicals. He suggests that they will add more readily to double bonds of alkenes or abstract H-atoms from hydrocarbons more readily than CH_3O or other alkoxy radicals.

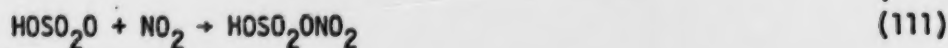




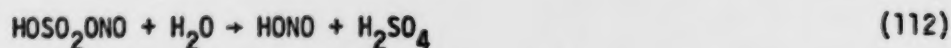
The thermal decomposition of the HOSO_2O radical to generate an HO-radical and SO_3 is endothermic by about 40 kcal and is probably unimportant in the atmosphere.



Alternatively the coupling of HOSO_2O with NO and NO_2 could occur to create nitrosylsulfuric acid in 110 or nitrylsulfuric acid in 111:



It has been suggested that HOSO_2ONO and $\text{HOSO}_2\text{ONO}_2$ will have large heats of condensation; they will be readily sorbed onto surfaces and exothermically hydrolyze to sulfuric acid and nitrous acid (112) or nitric acid (113).^{91,1}



The potential role of nitrosylsulfuric acid in the atmospheric chemistry of SO_2 - NO_x mixtures is of special interest since this compound can act as a strong nitrosating reagent which will form nitrosamines or nitrosamides by its reaction with amines and amides, respectively, under acidic conditions such as exist in sulfuric acid aerosol solutions. Nitrosylsulfuric acid has been the subject of several studies and much

speculation. Schoeder and Urone,⁹⁸ Bourbigot et al.,⁹⁶ and Canosa et al.⁹⁷ identified this compound among the products of the photooxidation of SO_2 - NO_2 -air mixtures. Presumably Farlow et al.⁹⁹ tentatively found two forms of nitrosylsulfuric acid (HOSO_2ONO and $\text{HOSO}_2\text{OSO}_2\text{ONO}$) in stratospheric aerosols through electron diffraction techniques. Cox and Derwent¹⁰⁰ studied the effect of SO_2 on NO and NO_2 formation in the photolysis of HONO , NO , NO_2 , SO_2 -air mixtures. In some experiments the aerosol formed was treated with water and nearly equal amounts of SO_4^{2-} (1.03 μmoles) and NO_3^- (1.20 μmoles) were detected; 0.02 μmoles of NO_2^- were found. The possible presence of nitrosyl or nitrylsulfuric acid-like compound ($\text{H}_x\text{SO}_y\text{NO}_z$) was suggested as a rationale for their findings.

Published evidence for the significant participation of HOSO_2ONO and/or $\text{HOSO}_2\text{ONO}_2$ in the photooxidation of SO_2 , NO_x mixtures in air is not compelling. In fact Niki et al.¹⁰¹ failed to find any infrared spectral evidence for HOSO_2ONO or $\text{HOSO}_2\text{ONO}_2$ formation in the photolysis products of the mixture: Cl_2 (20 ppm), H_2 (1000 ppm), SO_2 (20 ppm), and NO (5 ppm) in air (700 torr). See Figure 6; the spectra are for the aerosol products from the HO -radical induced, SO_2 oxidation in NO -containing (top) and NO , NO_2 -containing mixtures (bottom). These appeared to be nearly identical to the spectra of H_2SO_4 aerosol. Certainly the infrared bands attributed to HOSO_2ONO by Schroeder and Urone⁹⁸ (Figure 7) were not seen in the products. Hence Niki et al. concluded nitrogenous sulfuric acids do not serve as significant sinks for SO_2 and NO_x in the atmosphere. However there is a problem with integrity of the HOSO_2ONO reference spectrum of Schroeder and Urone. They found that HOSO_2ONO

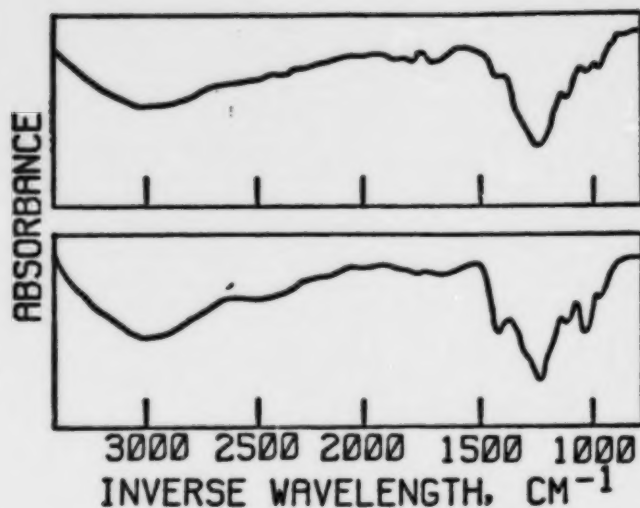


Figure 6. Aerosol spectra from the products of the SO₂ photooxidation in the presence of NO (top) and NO₂ (bottom); both spectra appear to be that of sulfuric acid-water aerosols.¹⁰¹

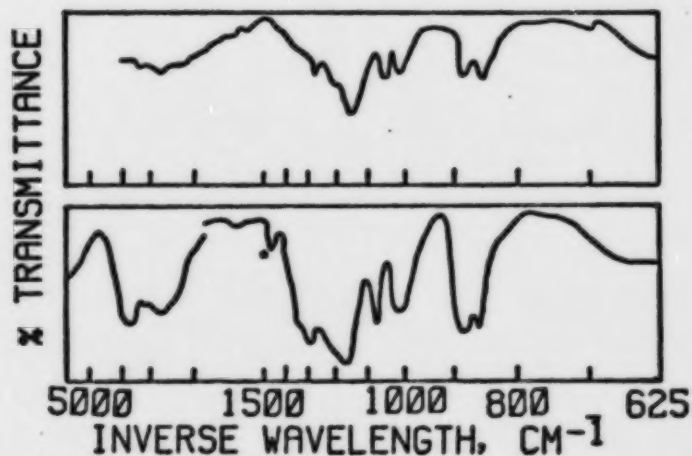
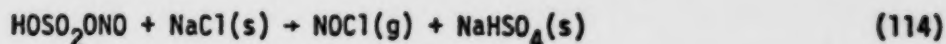
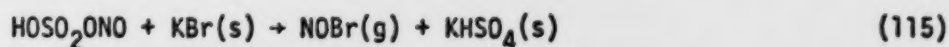


Figure 7. Infrared spectrum of "nitosylsulfuric acid" reported by Schroeder and Urone,⁹⁸ (top); spectrum of potassium bisulfate (bottom).

reacted with dry NaCl(s) to form NOCl and NaHSO₄(s):



However they then chose to employ KBr(s) as a matrix for the nitrosyl-sulfuric acid compound and reported the spectrum of this sample as that due to HOSO₂ONO; see Figure 7. They noted the similarity between this spectrum and that for KHSO₄(s), but since both compounds had the HOSO₂O-structure in common, they took this as evidence for the authenticity of the HOSO₂ONO sample. In retrospect it is clear that if NaCl(s) reacted with HOSO₂ONO then one would expect KBr(s) to react equally well. Indeed we find this is the case.¹⁰² Reaction 115 occurs rapidly and is completely analogous to 114:



It is not surprising that the spectrum reported by Schroeder and Urone is very similar to that for KHSO₄; since NOBr would be lost as a gas during their preparation procedure, the product left is KHSO₄(s). Other ultraviolet-visible spectra reported by Canosa et al.,⁹⁷ which were attributed to HOSO₂ONO (Figure 8), probably do not originate in this compound. The bands are identical to those of HONO, a hydrolysis product of HOSO₂ONO. Since the conclusion of Niki et al. that HOSO₂ONO is unimportant in the photooxidation of SO₂ was based upon the absence of features in their spectra which had been incorrectly attributed to HOSO₂ONO, the question remains as to the possible involvement of this compound.

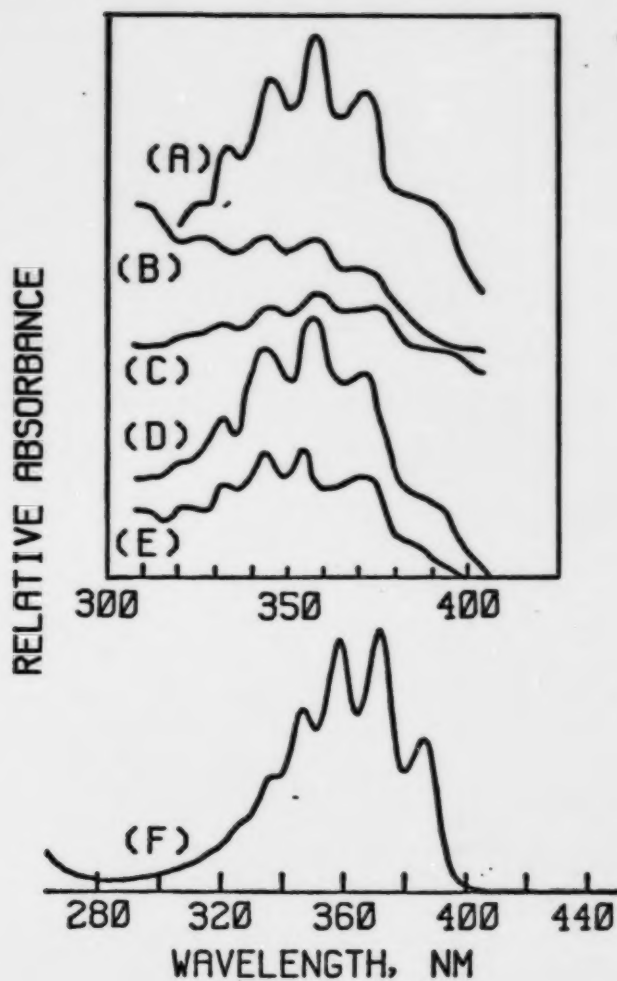


Figure 8. Ultraviolet absorption spectra of reaction products of Canosa et al.⁹⁷; ethyl nitrite in $\text{CF}_3\text{CHOHCF}_3$ (A); nitrosylsulfuric acid in $\text{CF}_3\text{CHOHCF}_3$ (B); nitrosylsulfuric acid in CH_2Cl_2 (C); $\text{SO}_3 + \text{NO}_2$ reaction product in CH_2Cl_2 (D); $\text{SO}_2 + \text{NO}_2$ photoreaction product (E); reference spectrum of HONO in aqueous acid solution (F).

Recently we carried out a series of experiments to characterize better the spectral properties of HOSO_2ONO and its solutions in H_2SO_4 - H_2O mixtures. HOSO_2ONO is a very hygroscopic compound which hydrolyzes readily to form sulfuric acid and nitrous acid. If it were produced in the atmosphere it is probable that it would soon become part of sulfuric acid-water aerosol solution, so the choice of such H_2SO_4 - HOSO_2ONO solutions for our study seemed logical. The spectral properties of pure HOSO_2ONO solid and its solutions in H_2SO_4 - H_2O mixtures should be reviewed here briefly. In concentrated H_2SO_4 solutions the spectral features are consistent with those anticipated for a solution of NO^+ and HSO_4^- ions. The solutions absorb in the near ultraviolet region, and both the magnitude and position of the maximum in the extinction coefficient are sensitive to the water content of the H_2SO_4 solutions; see Figure 9. These shifts are similar to those found by Bayliss et al. for solutions of NaNO_2 in aqueous H_2SO_4 .¹²⁸ The rate of hydrolysis of the HOSO_2ONO becomes significant in H_2SO_4 solutions which have greater than 30% by weight water present; reaction between NO^+ and water occurs to generate other species for these conditions; see Fig. 10. Absorption due to N_2O_3 is seen first as one dilutes a HOSO_2ONO - H_2SO_4 solution with water (see Figure 11), while the spectral features of HONO appear upon further dilution (See curve F of Fig. 8). The Raman spectrum of HOSO_2ONO in H_2SO_4 shows the characteristic bands due to NO^+ and HSO_4^- species.¹²⁹ In Figure 12 compare the spectral features of HOSO_2ONO - H_2SO_4 solution with those of an H_2SO_4 solution. The position of the NO^+ band is sensitive to the H_2O content of the H_2SO_4 solution; it shifts to lower energies as the H_2O content increases; see Figure 13. The infrared spectrum of the

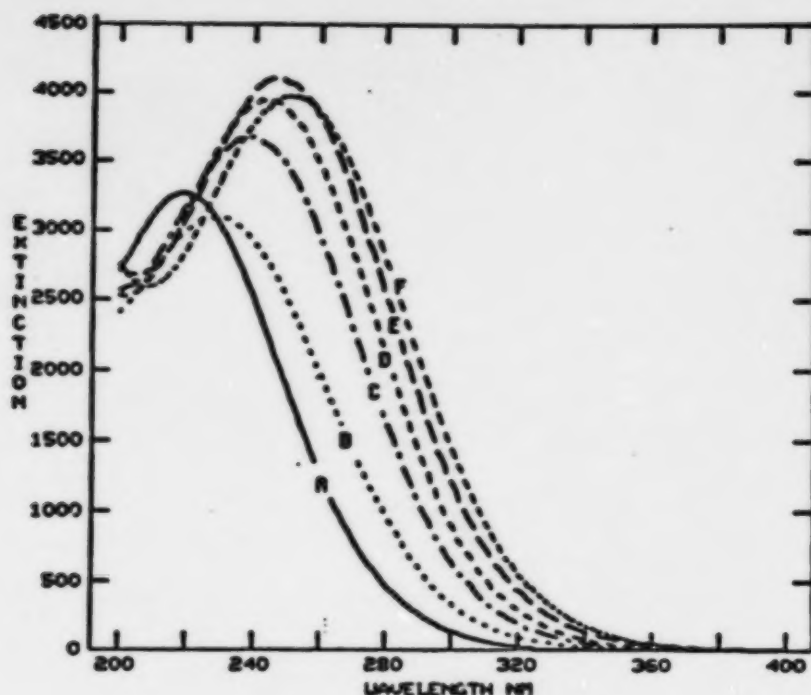


Figure 9. Ultraviolet absorption spectra of solutions of nitrosylsulfuric acid in H_2SO_4 - H_2O mixtures; weight percent H_2SO_4 : 95.60 (A); 90.29 (B); 84.74 (C); 78.78 (D); 72.12 (E); 64.69 (F).

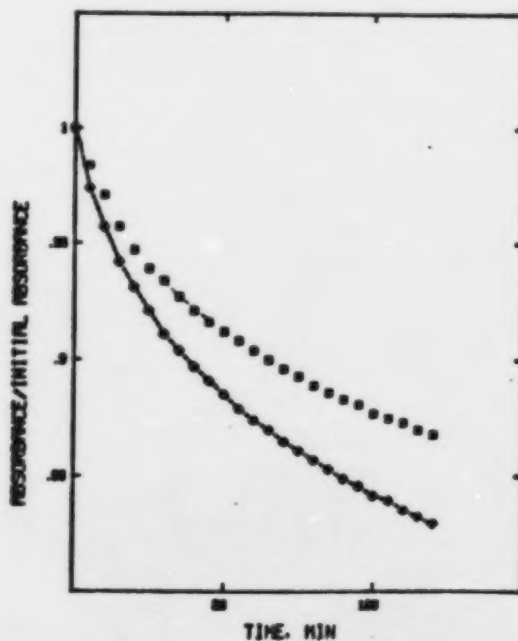


Figure 10. The change in absorbance of a nitrosylsulfuric acid-water solution (55.67% H_2SO_4) as a function of time; absorbance measured at 240 nm; hydrolysis of the nitrosylsulfuric acid leads to this change; temperature, 32°C (diamonds), 20°C (squares); data of Stockwell.¹⁰²

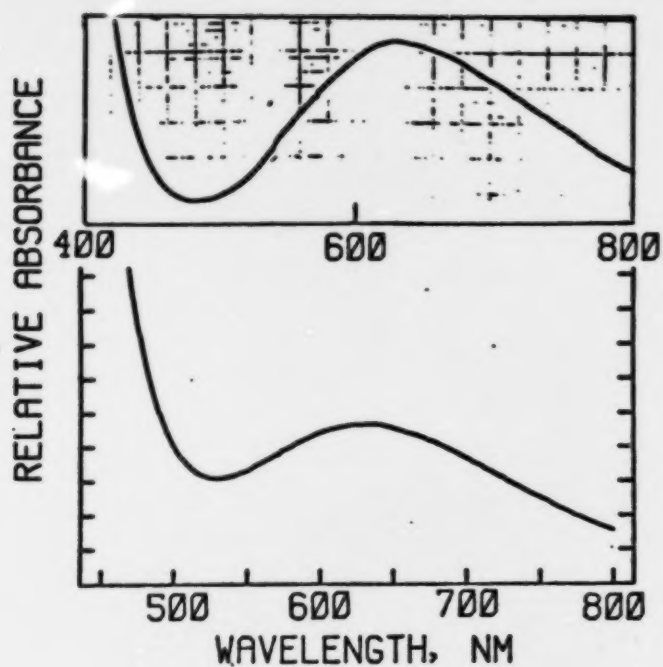


Figure 11. Absorption of the first product of HOSO_2ONO hydrolysis in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solution (top) and reference spectrum of N_2O_3 in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solution; data of Stockwell.¹⁰²

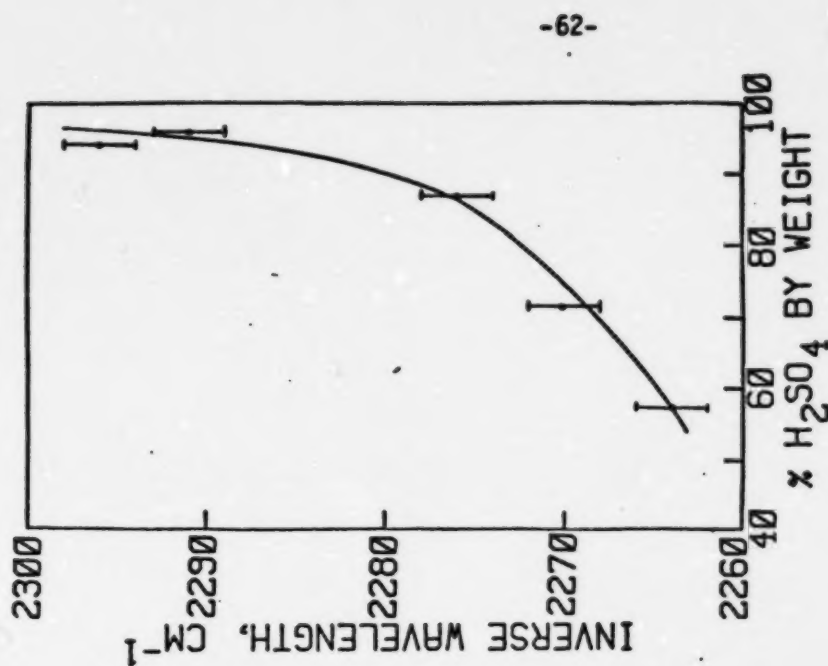


Figure 13. The variation of the vibrational frequency of the NO^+ band in HSO_2ONO in H_2SO_4 solutions of varied water content.

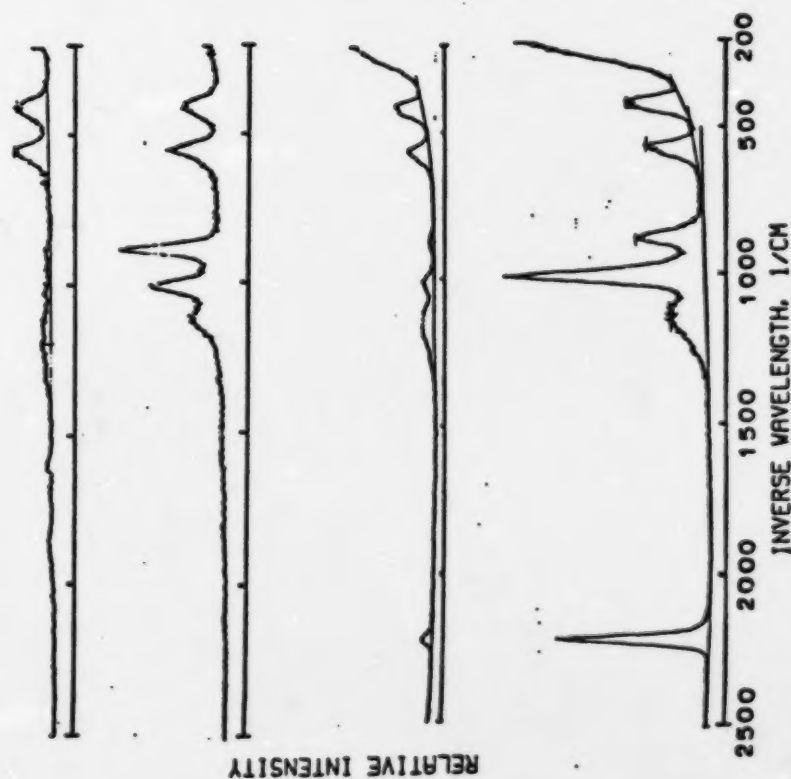


Figure 12. Raman spectra of HSO_2ONO in H_2SO_4 (87.0% by wt)- H_2O solution (bottom two spectra) and the pure H_2SO_4 - H_2O solution (top two spectra); the polarization of the filter in front of the detector was rotated by 90° in curves 1 and 3; data of Stockwell.¹⁰²

nitrosylsulfuric acid in H_2SO_4 is similar to that for H_2SO_4 but it has a weak, characteristic band due to the NO^+ ion, see Figure 14. These spectra are similar to those reported by Stopperka and Kilz¹⁰³ for N_2O_3 solution in H_2SO_4 , see Figure 15. Undoubtedly the two final solutions contain the same chemical entities although the methods by which they were prepared are very different.

The spectral features of HOSO_2ONO are such as to make identification of small quantities very difficult. The broad absorption features of HOSO_2ONO in H_2SO_4 in the $700\text{--}1400\text{ cm}^{-1}$ range are not easily resolved from those of H_2SO_4 , the positions and shapes of which are also somewhat sensitive to the water content²⁶; see Figure 16. Also the characteristic NO^+ band of HOSO_2ONO is so weak that one is seriously limited in its use as a means of detection at low levels. Furthermore, the rate of hydrolysis of HOSO_2ONO in the $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions becomes significant for solution containing less than 68% H_2SO_4 . Of course, H_2SO_4 aerosols which exist in the atmosphere near 25°C in contact with water vapor above about 3 torr of pressure have this composition. In view of all of these properties it is clear that the evaluation of the role, if any, that HOSO_2ONO plays in atmospheric $\text{SO}_2\text{--NO}_x$ chemistry will be most difficult to define.

We attempted experiments designed to help define the HO-radical SO_2 , NO_x mechanism in the atmosphere and the possible HOSO_2ONO participation in this¹⁰⁴. Mixtures of ppm concentrations of HONO, NO, NO_2 , SO_2 , and CO in N_2/O_2 mixtures at 700 torr were photolyzed to initiate the reactions. Introduction of water vapor with the HONO was unavoidable

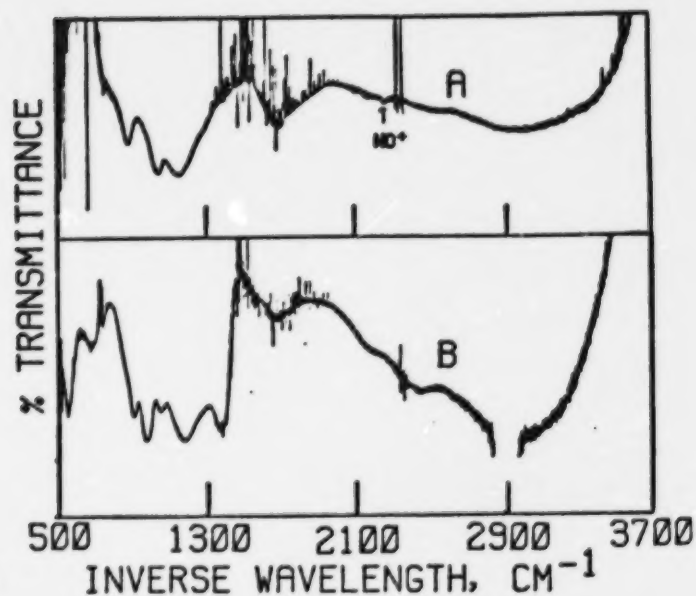


Figure 14. Infrared spectra of nitrosylsulfuric acid (A) and concentrated sulfuric acid (B); data of Stockwell;¹⁰² BaF₂ plates were used to hold the samples here.

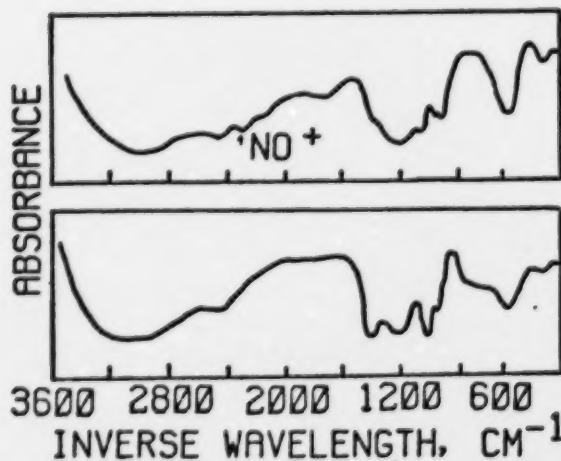


Figure 15. Infrared spectra of the N₂O₃-H₂SO₄ system (top) and sulfuric acid (bottom); data of Stopperka and Kilz.¹⁰³

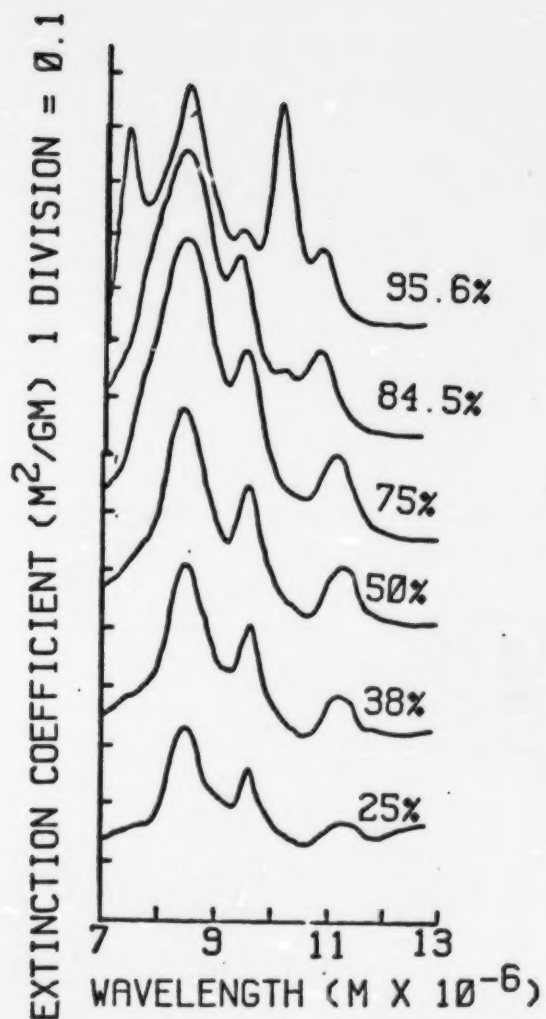


Figure 16. Calculated extinction coefficients for 1 micron sulfuric acid aerosol particles with varied amounts of water; number shown is the wt % H_2SO_4 ; data of reference 28; each curve has been shifted from the preceeding curve by 0.2 units on the y-axis.

with the generation procedure employed. Its amount could be estimated reasonably well through the long-path Fourier transform infrared equipment employed to follow the reaction; it varied from a low of about 2 torr in one experiment to a maximum of 8 torr in another. Aerosol absorbance at 878 and 894 cm^{-1} correlated well with SO_2 loss in experiments of high water content (Figure 17), and the aerosol was observed to be largely H_2SO_4 for these conditions. Figures 18 and 19 show the time dependence of the reactants and the major products formed in an experiment at 8 torr of H_2O . The CO_2 was formed during the experiment from the HO- CO reaction which was used to monitor the HO-radical levels. There are several features of the results which should be noted. The reactions stop as the light is turned off; dark reactions are unimportant. Even the aerosol is rather stable during the time span of the experiment. The nitrogen mass balance remains good throughout the experiment; there is no evidence of HOSO_2ONO among the products, although its detection by infrared is not sensitive and we could miss as much as 1 ppm of this compound. However, the sulfuric acid aerosol probably contained about 50% by weight H_2O for the conditions employed here (8 torr, H_2O), so the decomposition of any HOSO_2ONO formed would be rapid for these conditions ($\text{HOSO}_2\text{ONO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \text{ (aerosol)} + \text{HONO(g)}$).

In an experiment at the lowest water vapor concentration (2 torr) the results are somewhat different; see Figures 20 and 21. The bands due to the H_2SO_4 aerosol showed a delay in appearing, and, although the error is large, some deficiency in the nitrogen mass balance seems to be present in this experiment. For these conditions the stability of the possible HOSO_2ONO product in H_2SO_4 would be enhanced over that for the

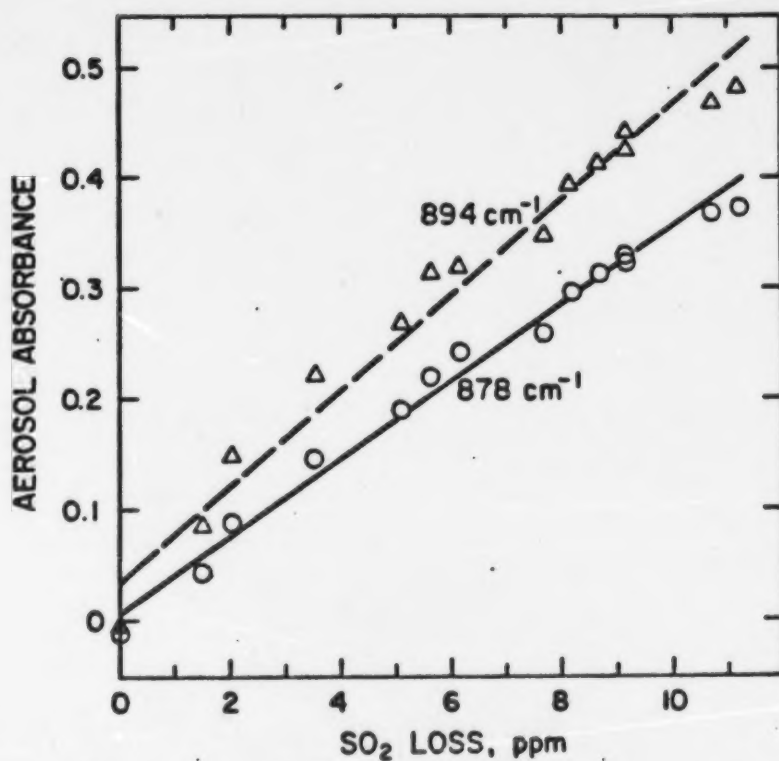


Figure 17. The aerosol absorbance at 878 and 894 cm^{-1} versus SO_2 lost in photooxidation of SO_2 ; aerosol appears to be $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions in this experiment at high H_2O pressure; data of Stockwell.¹⁰²

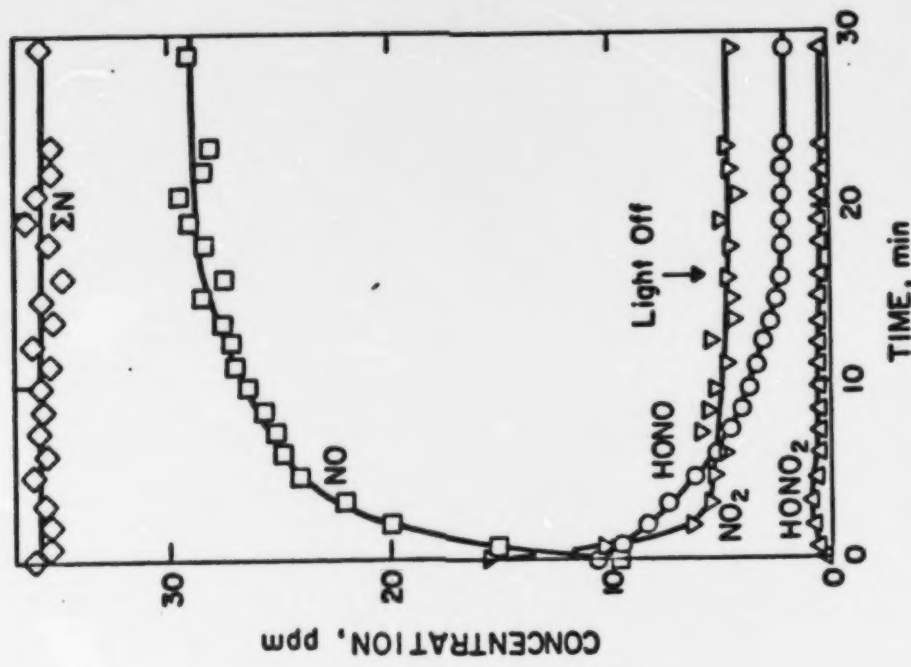


Figure 19. The time dependence of the nitrogen products and the mass balance for nitrogen from the HONO-HO₂-SO₂-CO-air mixture photolysis at high H₂O pressure; data of Stockwell.¹⁰²

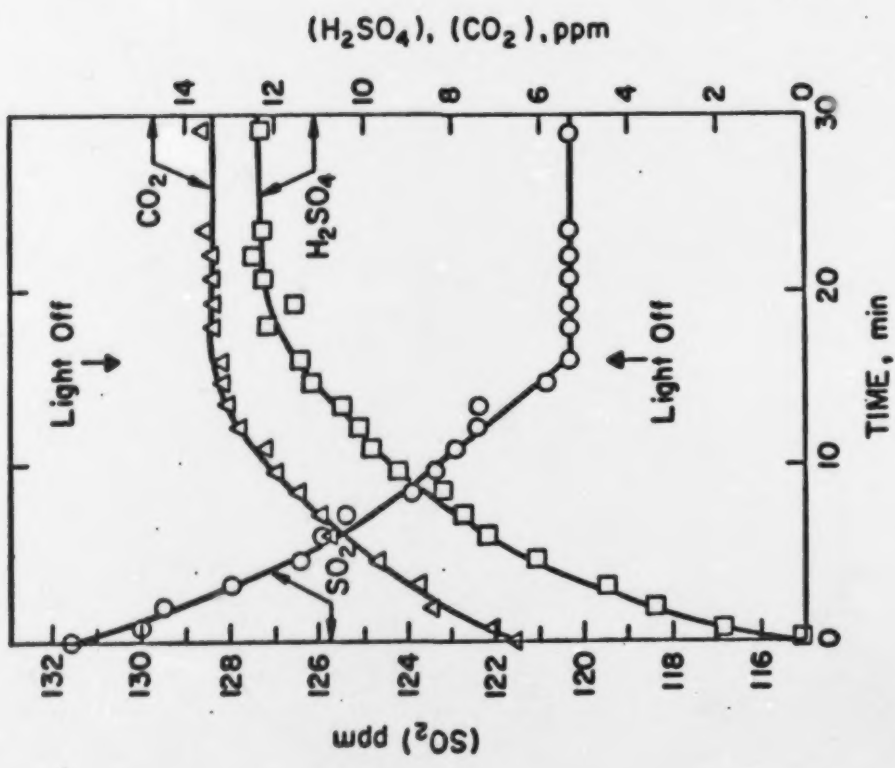


Figure 18. The time dependence of products of the HONO-HO₂-SO₂-CO-air mixture photolysis; data of Stockwell¹⁰² from runs at high H₂O pressure.

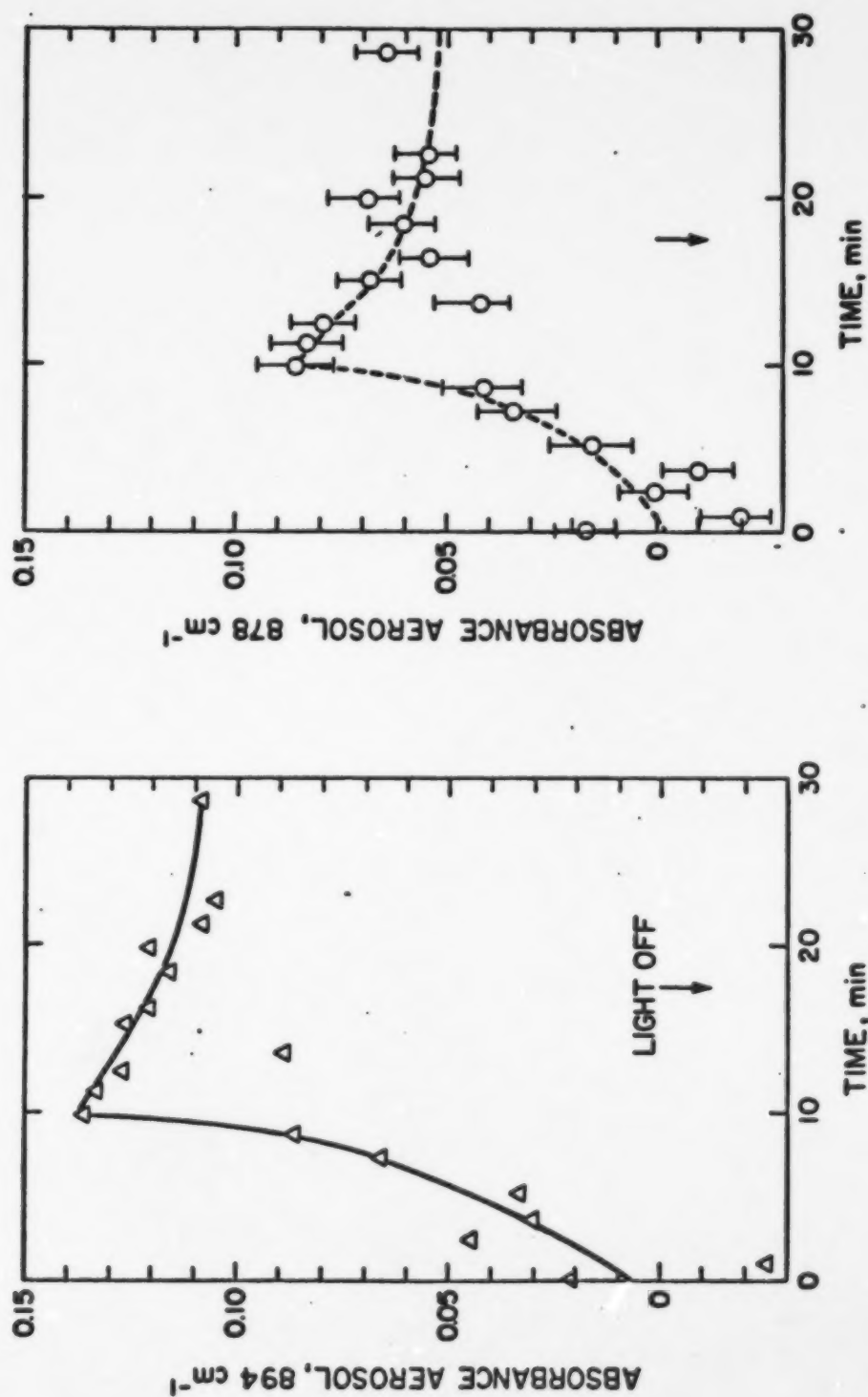


Figure 20. The time dependence of the absorbance of aerosol at 894 and 878 cm^{-1} from an experiment at low water pressure in the photolysis of HONO- NO_x - SO_2 -CO-air mixture; data of Stockwell.¹⁰²

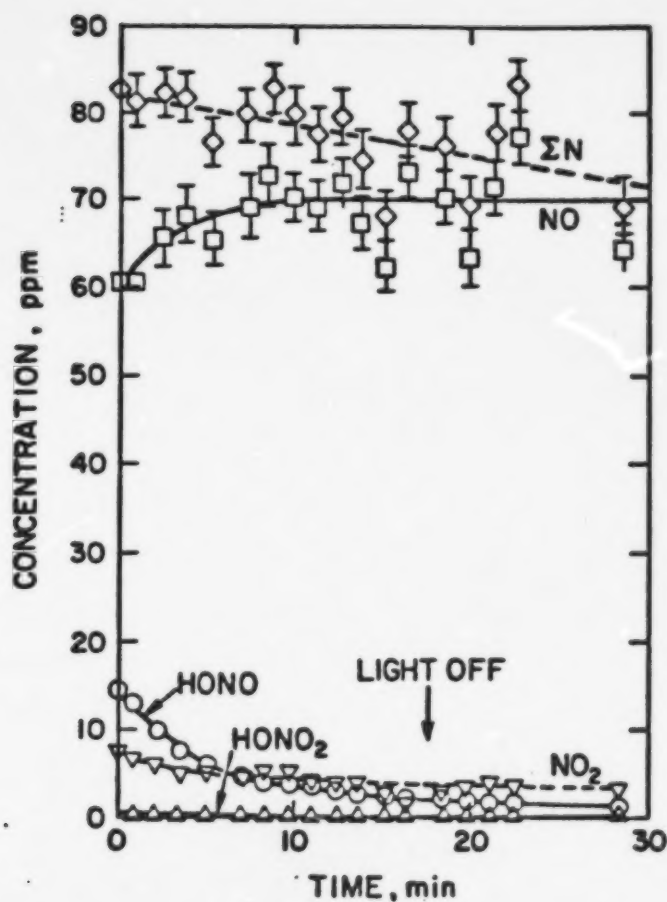


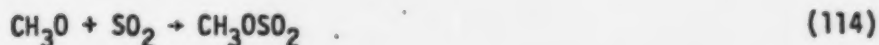
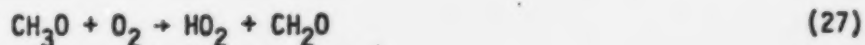
Figure 21. The nitrogen products as a function of time and the nitrogen mass balance from an experiment at low water pressure in the photolysis of HONO-NO_x-SO₂-CO-air mixture; data of Stockwell.¹⁰²

experiments at 8 torr of H_2O . However, there is still no direct evidence for the formation of $HOSO_2ONO$ here.

Very favorable conditions were present in these experiments for $HOSO_2ONO$ involvement and the occurrence of reaction 110 or possibly 111. $HOSO_2O_2$ and $HOSO_2O$ radicals should be present at high levels, and the high concentration of NO should insure frequent encounters between $HOSO_2O$ radicals and NO . If this reaction is occurring, then we must conclude, as did Niki et al., that the hydrolysis of $HOSO_2ONO$ and/or $HOSO_2ONO_2$ is very rapid for the conditions employed here. We are making further studies of this system at low H_2O levels to attempt to elucidate further the illusive reaction pathways for $HOSO_2O$ radical.

F. The Atmospheric Oxidation of SO_2 by Alkoxy Radicals

Recent studies of Kan et al.³⁶ demonstrate that the CH_3O radicals add to SO_2 readily. They studied the photolysis of dilute mixtures of CH_3ONO with varied O_2 , SO_2 , and N_2 at total pressures near 760 torr at $25^\circ C$. The competitive rates of CH_3O -radical reactions with O_2 , NO_2 , and SO_2 were determined. Taking $k_{27} = 6.1 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$, they estimated $k_{114} = 5.5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ at $25^\circ C$.



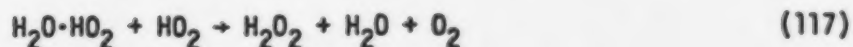
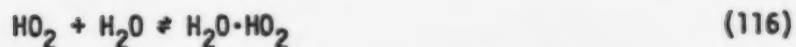
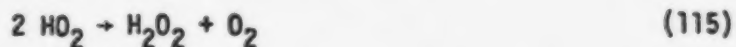
The final products of the reaction remain unproven, but the positions of the infrared absorption bands of one product were consistent with a species of molecular structure: CH_3OSO_2OH . However, reactions such as 114 are not expected to be important in the troposphere. The methoxy

radical and its higher analogues, C_2H_5O , C_3H_7O , etc., have very short lifetimes in the atmosphere, since the reactions with O_2 (27 and analogous reactions) dominate for the O_2 -rich air mixtures. The CH_3O is thought to be the longest lived of the series of alkoxy radicals, but even this radical has little chance to interact with SO_2 . Thus in air containing 50 ppb of SO_2 the fraction of CH_3O radicals formed in the air which survive to react with SO_2 is negligible, about 2×10^{-4} .

V. THE INFLUENCE OF THE HOMOGENEOUS GAS PHASE CHEMISTRY ON THE ATMOSPHERIC OXIDATION OF SO_2 IN RAIN WATER, AEROSOL SOLUTIONS, CLOUD WATER, AND GROUND WATER

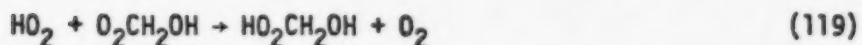
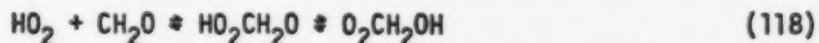
In the previous chapters of this book we have learned how SO_2 dissolved in cloud water or other solutions in the atmospheric environment can be oxidized to H_2SO_4 through the reactants ozone and hydrogen peroxide. Of course, both O_3 and H_2O_2 are products of homogeneous gas phase reactions, so it must be recognized that the gas phase and liquid phase pathways of acid generation in the troposphere are not completely independent.

The major sources of H_2O_2 in the gaseous troposphere are reactions 115 and 117 involving the HO_2 and the hydrated HO_2 radicals:



You will recall from our previous discussions that the complex $H_2O \cdot HO_2$ represents only a few percent of the total HO_2 concentration in the

atmosphere; however, the rate constant inequality, $k_{117} > k_{115}$, insures that its role in H_2O_2 formation is not insignificant. Of course, if an aqueous phase is available to the gaseous H_2O_2 product, then this compound will end up largely in that phase because of the large Henry's law constant for H_2O_2 in water. In the polluted atmosphere there is a strong competition for the HO_2 radicals through reactions 24, 118, 119, and possibly others:



Of course, the efficiency with which H_2O_2 is generated in the polluted troposphere through 115 and 117 is a complex function of the $[NO]$ and $[CH_2O]$ as well as the concentrations of CO , hydrocarbons (RH) and aldehydes ($RCHO$) from which the HO_2 radical is derived; see reactions 19, 20, 28, etc. Simulations which we have made of the complex chemistry of the polluted troposphere show that with a highly polluted air mass ($[NO_x] = 100$ ppb, $[RH] = 500$ ppb, $[RCHO] = 30$ ppb), H_2O_2 development is unimportant until the $[NO]$ has been depleted late in the day. However, for conditions more typical of a non-urban air mass, it is not uncommon to have very low NO_x levels (~ 1 ppb) and somewhat higher $[RH]$ and $[RCHO]$ levels; then H_2O_2 generation can begin early in the day. When $[NO_x]$ is very high (100 ppb) and $[RH]$ and $[RCHO]$ are low initially ($[RH] = 50$ ppb, $[RCHO] = 3$ ppb), little H_2O_2 forms. However, with small levels of all of the pollutants, H_2O_2 formation in 115 and 117 can be significant.

O_3 production in the troposphere follows a somewhat different pattern. Its development is most favored in the highly polluted atmosphere although significant concentrations (0.08 ppm) may be generated in relatively clean urban and rural atmospheres.

One may conclude from these limited observations that conditions of low NO_x and high hydrocarbon and aldehyde impurity levels favor H_2O_2 formation, while those of relatively high NO_x , RH, and RCHO favor high O_3 generation rates. Now if the homogeneous air masses containing the preformed H_2O_2 and O_3 encounter cloud water, rain water, high aqueous acid aerosol levels, etc., then a solution phase pathway for H_2SO_4 formation is favored as well. Since the optimum impurity levels for O_3 generation can be very different from those for H_2O_2 formation, the components of the H_2O_2 and O_3 oxidation of SO_2 (HSO_3^-) in the solution phase will not proceed exactly in phase with fixed fractions occurring by each pathway. The rates of SO_2 oxidation to acids in the homogeneous gas phase oxidation and those of the solution phase reactions will depend upon two quite different, complex functions of the pollutant concentrations. However, it is clear that the two processes are not entirely independent.

VI. THE MECHANISM AND RATES OF THE ATMOSPHERIC OXIDATION OF THE OXIDES OF NITROGEN

The homogeneous formation of nitric acid within the troposphere appears to be a much less complicated, better understood process than the mechanisms leading to H_2SO_4 from SO_2 . We have observed previously the important role of the HO_2 and RO_2 radicals in oxidizing NO to NO_2 in

reactions 24-36, and the part that the HO-radical plays in initiating the chain reactions of hydrocarbons and aldehydes which generate these species. During the daylight hours, these reactions proceed at rates of NO to NO₂ conversion which are very large compared to that for the slow termolecular reaction of NO with O₂:



Reaction 120 requires many hours or even days for the significant oxidation of NO to NO₂ when NO is present at typical low levels found in the troposphere.

The major source of HONO₂ formation through gas phase reactions is 121 involving the HO-radical:



A great variety of experimental evidence supports this view. There is little we can gain for our present purposes in reviewing here the original data related to 121. The most recent studies¹⁰⁵⁻¹⁰⁷ of this reaction and the reviews of the previous work suggest that estimates of k_{121} are well characterized for conditions applicable to the troposphere ($\text{M} = \text{N}_2$). In his review of the kinetic data for reaction 121, Anderson¹⁰⁷ recommended that the low pressure, third order constant for 121 be evaluated from relation 122:

$$k_{111}(121) = 2.3 \times 10^{-30} (T/298)^{-2.9} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1} \quad (122)$$

He also recommended that at the high pressure limit the apparent second

order constant be derived from equation 123:

$$k_{II(-)}(121) = 1.2 \times 10^{-11} (T/298)^{-1.6} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1} \quad (123)$$

These values can be used together with the Troe expression¹²² to estimate $k_{II}(121)$ values within the important atmospheric regions in which transition between second and third order kinetics for this reaction occurs¹⁰⁸:

$$k_{II}(121) = \frac{k_{III}[M]}{1 + k_{III}[M]/k_{II(-)}} 0.8 \{ (1 + [\ln k_{III}[M]/k_{II(-)}])^2 \}^{-1} \quad (124)$$

Using these kinetic data we have made the plot shown in Figure 22 of the effective second order rate constant for various altitudes and conditions of $[M]$ and temperature characteristic of the standard atmosphere. The same general trends in $k_{II}(121)$ with altitude are seen as observed for the HO-SO_2 reaction rate constant $k_{II}(85)$ in Figure 5, but the $k_{II}(121)$ values are roughly a factor of ten larger than the $k_{II}(85)$ values for the troposphere.

A second homogeneous mode of HONO_2 formation is that involving N_2O_5 :



It is very difficult to sort out the homogeneous component of this reaction in laboratory experiments, since the $\text{N}_2\text{O}_5\text{-H}_2\text{O}$ reaction at a moist cell wall can be more important than the homogeneous reaction for most experimental systems. Morris and Niki¹⁰⁹ reported an upper limit to this constant: $k_{123} \leq 1.3 \times 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. For the

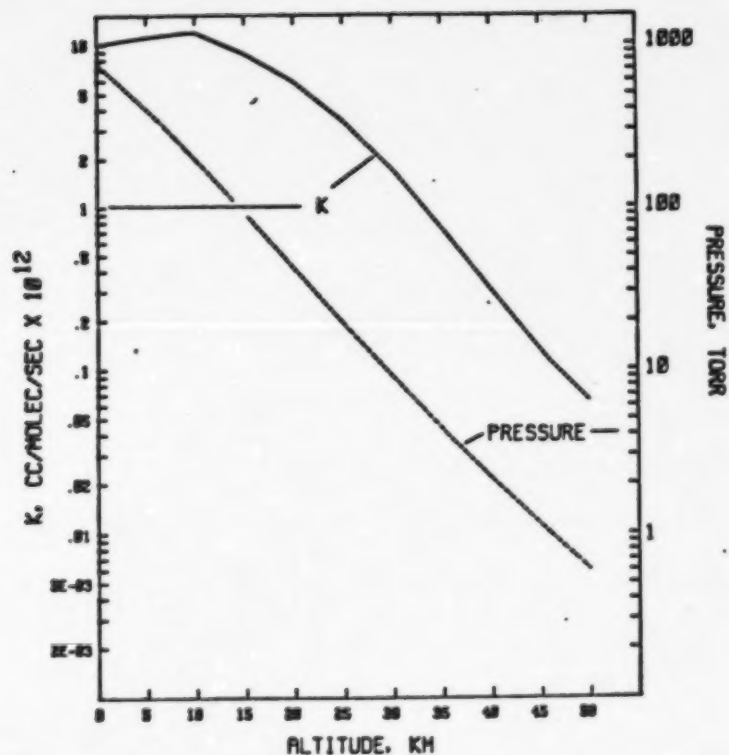


Figure 22. Variation of the apparent second order rate constant for reaction 121, $\text{HO} + \text{NO}_2 (+\text{M}) \rightarrow \text{HONO}_2 (+\text{M})$, as a function of altitude; calculated from the equations 122-124 for the conditions of pressure and temperature defined for the standard atmosphere.⁸⁶

theoretically expected N_2O_5 concentrations within the troposphere ($[\text{N}_2\text{O}_5] = 2.5 \times 10^9 \text{ molec cm}^{-3}$), the rate of 125 is insignificant compared to 121.

VII. THE THEORETICAL RATES OF SO_2 AND NO_2 CONVERSION TO H_2SO_4 AND HONO_2 THROUGH GAS PHASE REACTIONS IN THE TROPOSPHERE

The major homogeneous processes for SO_2 and NO_2 conversion to H_2SO_4 and HONO_2 , respectively, are governed by the rates of reactions 85 and 121. Obviously these depend on the reactant concentrations, $[\text{NO}_2]$, $[\text{SO}_2]$, $[\text{HO}]$, as well as the rate constants for these reactions. It is clear that we still require a knowledge of the $[\text{HO}]$ in the troposphere to couple with the rate constant and $[\text{NO}_2]$ and $[\text{SO}_2]$ data to obtain reasonable theoretical estimates of the minimum rates of the gas phase generation of the H_2SO_4 and HONO_2 acids. Although the direct measurement of $[\text{HO}]$ within the troposphere is very difficult, there are both theoretical and experimental estimates of this quantity which are of some value for our considerations here. These are summarized in Table V. We have excluded the early estimates based upon laser induced fluorescence of the HO-radical since the generation of HO by the probing laser beam itself was then an unrecognized problem. Data based upon the ^{14}CO -chemical method of Campbell and co-workers¹¹⁰, the laser induced fluorescence data of Wang and his colleagues¹¹¹, and the HO-absorption data of Ehhalt and co-workers¹¹² are all reasonably consistent among themselves and with theoretical estimates based upon computer models of the complex atmospheric chemistry¹¹³. We may use these data to make reasonable estimates of the gas phase oxidation rates for SO_2 and NO_2 which give us a feel for the potential of reactions 85 and 121 to develop the

Table V. Measured and Theoretical Estimates of the [HO] in the Troposphere

<u>[HO], molec cm⁻³</u>	
A. Experimental Methods	
1) Chemical Method: $^{14}\text{CO} + \text{HO} \rightarrow ^{14}\text{CO}_2 + \text{H}$ (Campbell et al. ¹¹⁰)	
Pullman, Wash. (46.7°N, 770 m)	$(5.8 \pm 2.4) \times 10^5$
New Zealand (44°S, 1030 m)	$(1.1 \pm 0.4) \times 10^6$
Tennessee (Rural, 36°N, 270 m)	$(1.9 \pm 0.7) \times 10^6$
Los Angeles (34°N, 270 m)	$(5.0 \pm 1.2) \times 10^6$
Arizona (Desert, 37°N, 2300 m)	$(57 \pm 23) \times 10^6$
2) Laser Induced Fluorescence, 2820.7 Å excitation, 3090 Å emission, 3020 Å N ₂ Raman (Wang et al. ¹¹¹)	
Niwot Ridge, CO (3048 m)	$(40 \text{ to } 6) \times 10^6$
Los Angeles, CA (11886 m)	$(2.5 \pm 2) \times 10^6$
SanBernadino, CA (10057 m)	$(20 \pm 6) \times 10^6$
SanDiego, South, CA (10667 m)	$(10 \pm 4) \times 10^6$
Denver, CO (10057 m)	$(1 \pm 3) \times 10^6$
3) Absorption Spectroscopy, 3079.95 Å (Ehhalt et al. ¹¹²)	
Jülich, Germany (51°N)	$(11 \pm 6) \times 10^6$
Usually	$(6 \pm 3) \times 10^6$
B. Theoretical Estimates of [HO] in the Urban and Rural Troposphere	
Typical recent estimates found in simulations of Calvert, Demerjian, Seinfeld, Niki, Graedel, Isaksen, etc., and their co-workers:	
Daytime maximum (Summer, 40°N)	about 9×10^6
Daytime maximum (Winter, 40°N)	about 2×10^6
Nighttime values less than	about 2×10^5
(Values are sensitive to ultraviolet solar irradiance at point of interest, levels of impurities, NO, NO ₂ , RH's, RCHO's, etc.)	

ingredients for "acid rain". At high HO-radical concentrations, seemingly characteristic of midday sunny skies in the summertime, about $9 \times 10^6 \text{ molec cm}^{-3}$, we anticipate from our selected rate constant data that SO_2 will oxidize at a rate of $\sim 3.7\% \text{ hr}^{-1}$ through HO-radical attack in reaction 85. Rates of HONO_2 generation are expected to be about $34\% \text{ hr}^{-1}$ for these conditions. The somewhat lower midday solar intensities typical of the winter months for which $[\text{HO}] = 2.4 \times 10^6 \text{ molec cm}^{-3}$, lead to rates of about $1\% \text{ hr}^{-1}$ for SO_2 and about $18\% \text{ hr}^{-1}$ for NO_2 . Of course, these rates are expected to track the $[\text{HO}]$ during the day and drop rapidly to near zero during the nighttime hours.

We must remember when making such estimates for the gas phase SO_2 oxidation rates that other yet unevaluated contributions from the alkene- O_3 products, the CH_3O_2 -radical, and probably other unidentified reactants may contribute to the total SO_2 oxidation rate as well. However, the theoretical rates given here for the HO-reactions alone appear to match reasonably well those observed in SO_2 urban plumes¹¹⁴⁻¹²⁴. Certainly a large part of the observed oxidation in the cloud-free ambient troposphere during the daylight hours, arises from the HO- SO_2 reactions. The conversion rates for NO_2 observed by recent workers is also consistent with the estimates presented here.¹²⁵

One should not be so naive as to think that we now understand the gas phase atmospheric chemistry of SO_2 and NO_2 , but at least a good start toward this goal appears to have been made by the scientific community.

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